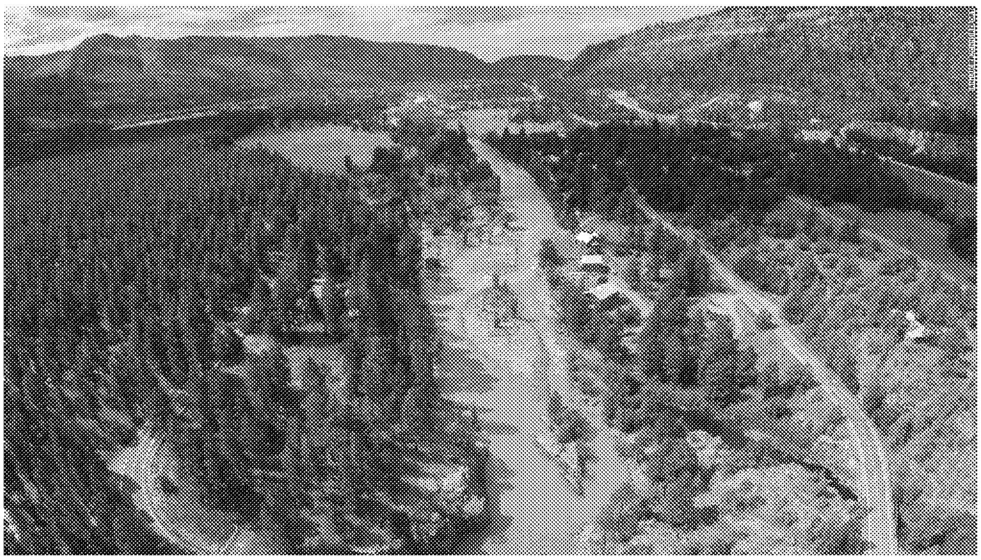
REVIEW DRAFT

Analysis of the Transport and Fate of Metals Released From the Gold King Mine in the Animas and San Juan Rivers

September 29, 2016



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List of Abbreviations

BOR	Bureau of Reclamation
CDPHE	Colorado Department of Public Health and Environment
DOI	U.S. Department of the Interior
EPA	U.S. Environmental Protection Agency
GKM	Gold King Mine
MSI	Moutain Studies Institute
NMED	New Mexico Environment Department
NNEPA	Navajo Nation Environmental Protection Agency
RK	River kilometer
SUIT	Southern Ute Indian Tribe
UDEQ	Utah Department of Environmental Quality
UMUT	Ute Mountain Ute Tribe
USGS	U.S. Geological Survey
USEPA	U.S. Environmental Protection Agency

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Executive Summary

On August 5, 2016, 3,000,000 gallons of acid drainage dammed within the abandoned Gold King mine in the San Juan Mountains of southwestern Colorado was released into a small headwaters tributary after accidental breaching of the plugged mine entrance. The release quickly traveled through Cement Creek that joins the Animas River13 km downstream in Silverton, CO. The mine waters had very low acidity and a high concentrations of potentially toxic metals. Only 2,800 kg of metals including metals such as iron, aluminum, and trace metals including lead, arsenic, copper and zinc spilled from the mine itself. The explosiveness of the release picked up a considerable amount of additional metals outside the mine entrance and in the 12.5 km it travelled before joining the Animas River. We estimate that ultimately 490,000 kg of a mixture of metals dominated by iron and aluminum was released into the Animas River within about an 8 hour period. Potentially toxic metals delivered in large amounts to the Animas River included lead, arsenic, copper, zinc, and cadmium. There was virtually no mercury in the release. Most of the metals were in particulate form but 15,000 kg of dissolved metals was also part of the mixture.

The Gold King release was small relative to the metals load observed over the course of a year from this area that is plagued by acid mine drainage contamination, but it was a significantly high concentrations and mass of metals input to the river at one time. The release was also different than ongoing contamination in that it was mostly colloidal/particulate metals eroded from a large mine waste pile outside the mine and from the streambed, rather than dissolved metals slowly leaked with groundwater or mine discharge directly to streams. The large mass of particulate metals was not usual in the acid mine drainage that characterizes the headwaters of the Animas River, except during high flows when contaminants are mobilized with bed sediment.

The release traveled as a coherent plume of concentrated metals mixing with the river flow over an 8-day period through 550 kilometers (370 miles) of the Animas and San Juan Rivers before ultimately reaching Lake Powell that fills part of the Grand Canyon. Water quality modeling was used to pinpoint travel characteristics and Gold King plume mass and concentrations with good agreement with observations and water sampling. The release crossed three states (Colorado, New Mexico and Utah) and three tribal reservations (Southern Ute Indian Tribe, Navajo Nation and the Ute Mountain Ute Tribe) and multiple communities along the way. EPA worked with state agencies, tribes and local communities through its Unified Command Center in Durango, CO to curb water use and provide alternative sources during the weeks following the release.

The plume was very chemically active in the first 100 km and 36 hours of travel. The low pH of the water that arrived with the plume from Cement Creek (pH about 3.5) was neutralized with mixing with the more alkaline Animas River that also carried 4 times the flow. The iron and aluminum in the mix reacted with oxygen increasing the pH and triggering chemical reactions that would form the iron and aluminum oxide colloids that gave the river an intense yellow color that was visible as the plume passed through 250 km of river. Other trace metals were sorbed into the colloids and precipitates also turning them to particulate form. Transformation to solid form reduced toxicity for many metals for many uses but increased toxicity for some.

As the plume traveled metals concentrations were diluted with incoming flow of waters from joining streams. Some of the iron and aluminum oxide colloids traveled suspended in the water for a long distance while a considerable mass of amorphous precipitates aggregated and deposited within the slower areas within the flowing stream and along the channel margins. The mass in transport was a mix of sediment, colloidal liquid (a texture like paint), aggregated precipitates and sludge. As the plume travelled, 90% of the metals mass was deposited within the Animas River and along the channel margins, with the majority trapped in the bed of the river between Silverton and Durango.

The plume had high concentrations of metals through the first 100 km of travel (source to Durango). The plume required from 8 to 48 hours to pass each location, stretching in length as drag from the river bed slowed the movement of some of the load. However, the majority of the mass and highest concentrations traveled in a central core within the plume that passed within about 10 hours.

Metals are natural components of soils and present in minute quantities in water. High levels of metals can be detrimental to human, terrestrial, and aquatic life. States and tribes have adopted water quality criteria that identify safe concentrations that protect life ingesting or exposed to water in various ways, such as drinking, recreational contact, and irrigation. Criteria also specific safe levels for aquatic life. Dissolved metal ions are readily reactive and many water quality criteria target dissolved metals. Particulate metals are also detrimental for some beneficial uses of water and organisms and criteria also specify some total metals such as aluminum.

Water quality criteria defined for various water uses were exceeded in some locations as the plume passed, especially in the upper Animas River closer to the mine source. Importantly, most metals did not exceed any criteria at any location. Agricultural criteria for copper, lead, and manganese were exceeded to 132 kilometers from source, including Durango and the Southern Ute Indian Tribe reservation.. Duration of water quality exceedances were short as the plume moved quickly. The EPA coordinating with states, tribes and local municipalities curtailed the use of water for drinking, irrigation, livestock watering, and recreation as the plume for a number of days to prevent exposures. Dilution and chemical reactions largely limited the spatial extent of significantly elevated concentrations to the upper Animas River.

Aquatic and terrestrial biota could not escape the plume. Acute criteria for aquatic life for aluminum were exceeded for up to 6 hours in the Animas River to the Colorado border at 147 kilometers from source. The duration was less than the 96 hour exposure built into the criteria. There were no reported fish kills and post event surveys by a variety of organisms have indicated other aquatic life did not appear to have suffered harmful effects from the plume. Monitoring continues to determine if there will be longer term chronic impacts from deposited metals beyond the effects of acid mine drainage known to impair parts of the watershed from historic mining activity. Bioaccumulation modeling conducted in this study support that fish and aquatic biota likely took up metals as the plume passed but excreted it over the next 15 days without lasting harmful effects to the organisms.

The metals that may have had the largest effect on water quality were aluminum, lead, and iron due to their predominance in the release load. These metals were particularly abundant in the plume and triggered exceedances of one or more water quality criteria along the rivers. Variation in exceedances reflect differences in criteria among states and tribes. Particulate (total) lead was detected most frequently.

Most of the metals, now in a solid form were deposited in the Animas River and just some entered the San Juan River at high enough levels to detect from background. Once the plume joined the San Juan River, the Gold King plume was swamped by the metals naturally associated with the high sediment loads that are characteristic of the San Juan and prevalent during plume passage as water was released from the Navajo Dam to help mitigate effects of the Gold King release. Metals are present in very low concentrations in the bed sediment of the San Juan River, especially compared to the sediments of the Animas, but the volume of sediment carried during moderate and high flows brings sufficient amounts of the trace metals into the water column to exceed water quality (especially tribal criteria) along with the most abundant aluminum and iron metals. During the plume, excess lead could be detected for some distance along the San Juan, and many of the tribal water quality criteria applicable to the San Juan River were triggered for this metal.

Gold King plume mass could have been deposited throughout the length of affected rivers, and there are many reports and photographs of residue. Modeling supported by monitoring data suggest that the vast majority was deposited in the upper Animas River between Silverton and Durango, with a lesser mass settled in the lower Animas River between Cedar Hill and Farmington, New Mexico. There also appeared to be deposits along a length of the San Juan River located immediately downstream of the confluence with the Animas in the Farmington area.

Although a large amount of Gold King material was deposited, especially in the headwaters, the metals deposits could not be distinguished in content or mass from those already in the streambed that store the legacy of a century of mining and ongoing AMD contamination. Metals concentrations in streambed sediments was not statistically different from pre-event conditions where there was sufficient data to compare.

It has been an ongoing concern that deposited metals would degrade water quality after the plume passed, or that deposited plume sediments would remobilize during higher flows and generate a second wave of contamination through the system. EPA, states, and tribes have monitored water and sediments intensively in the months following the release to evaluate post-event effects.

Post plume adjustments to the chemistry of the deposited minerals could be expected. The deposited precipitates were likely a mix of incipient and more stable minerals with different degrees of chemical stability. Deposits were not sampled for their geochemistry and mineralogy that would provide this study more complete understanding of the post event chemistry. Some of the minerals that probably formed, such as gypsum (a calcium sulfate mineral), would likely redissolve under different pH conditions. The majority of the deposits were likely iron and aluminum oxides. Once deposited, these would undergo "aging" and ripening as their structure internally organizes toward long term chemical stability.

The Gold King mine metals deposits were somewhat different than the ongoing contamination that affects the Animas River headwaters near Silverton. Some of the deposits were "sludge" formed from the aggregated colloids, some was colloids painted onto rocks, and some was precipitated aggregates settled into the streambed. A major question to address was under what conditions did metal deposits that had a variety of properties remobilize potentially creating a second wave of effects.

During the months after the release, concentrations of metals of concern such as lead, copper, zinc, arsenic, and cadmium did not generally statistically change relative to pre-event conditions where there was sufficient data for comparisons, suggesting return to pre-event conditions. However, statistical analyses indicated that post event geochemical reactions were taking place within the deposited material through the fall months, primarily involving iron and aluminum and that make up most of the mass with spatially variable effects on metals in water and sediments. Temporal changes to deposited material varied within the rivers, and were significant in some, especially in the first 3 weeks after the release. In all cases, metal concentrations declined from high levels observed immediately after the release, but the timing and dynamics of declining concentrations varied locally.

There are hundreds of water supply wells in the floodplain aquifers of the Animas River, ranging from continuous larger pumping wells (the community wells) to the small pumpers (the domestic/household wells) and there were concerns about the potential vulnerability to the Gold King plume on groundwater. Groundwater modeling suggested that only a handful of these wells potentially source water from the Animas River given their low pumping rates and general movement of water from surrounding topography towards the river. In some locations, the river feeds water into the adjacent floodplain, creating greater vulnerability to river metal concentrations. Whether any given reach of the Animas River is either gaining or losing is site specific and temporal. One community well located within 35m of the mid Animas River floodplain near Baker's Bridge had a chemical signal of some dissolved metals; we could not reject the hypothesis that this signal may have been associated with the GKM plume. But the observed breakthrough time was earlier than suggested by the computer simulations. The raw well water concentrations were below Federal drinking water action levels.

A treatment facility has been constructed in the North Cement Creek area that now captures and treats effluent from the Gold King Mine as one of numerous mines in the areas leaking acid mine drainage. Post-event monitoring shows that metals concentrations remain very high in Cement Creek but that colloidal/particulate metals are more prominent, possibly reflecting the treatment.

In the mid Animas, metals in the streambed and water declined somewhat from historical levels, suggesting that deposited aluminum and iron oxides continued to scavenge dissolved metals from the water after the release in the fall months, acting like a sponge. Gold King deposits appeared to shed low concentrations of dissolved aluminum and iron and trace metals into the lower Animas River as concentrations in the water column were elevated relative to pre-event conditions for several weeks after the release. Adjustments were statistically detectable but below water quality criteria thresholds. The dissolved metals from the lower Animas subsequently moved into the San Juan River where they increased concentrations in proportion to Animas flow. Once in the San Juan, the dissolved aluminum and iron are conserved and appear to pass through the length of the San Juan without change of deposition. On average iron and aluminum changes have not increased metals to adverse levels relative to water quality criteria applicable to the San Juan River. They also have not affected the concentrations of other trace metals to a detectable level.

The spring snowmelt of 2016 was the first high flow event that could flush Gold King deposits from the upper reaches of the Animas since the release occurred in August 2015. Spring snowmelt in 2016 was robust in the headwaters of the Animas and average through the Animas lower reaches and the San Juan River. Water and sediments were sampled through the 6-week period by EPA, states and tribes. Concentrations of a number of metals were elevated during spring runoff and could be statistically detected above what is normally carried in the river at high flows for some metals. Elevated concentrations were generally small but sufficient to account for the metals deposited during Gold King during the month that flow was elevated above the level observed during the release. Patterns in bed sediment changes over the snowmelt season as flow rose and fell suggested that Gold King deposits were mobilized from the areas of heaviest deposition in the middle Animas and redistributed downstream with some depositing in the lower Animas and the San Juan and some carried through the system.

CHAPTER 1: OVERVIEW

More than 50,000 inactive hard-rock mines on public lands and many more on private lands have left a legacy of acid drainage and toxic metals contamination across mountain watersheds in the western United States (BLM 2007). More than 40 percent of the watersheds in or west of the Rocky Mountains have headwater streams in which the effects of historical hard-rock mining are thought to represent a potential threat to human and ecosystem health through the persistent release of acidity and metals into water bodies (von Guerard et al. 2007).

Figure 1-1.

One of those areas is the headwaters of the Animas River that originates in the San Juan Mountains in southwest Colorado that lies within the southern extent of the Colorado Mineral Belt (Figure 1-1). The geologic stratigraphy of this area consists of a Precambrian crystalline basement overlain by Paleozoic to Tertiary sedimentary rocks that are capped by a thick sequence of Tertiary volcanic rocks (Luedke and Burbank 1999).

In a series of regional volcanic eruptions that took place during the late Paleogene (28-23M years), magma intruded into a northeasterly striking shear zone, Over geologic time, hydrothermal processes altered the pre-existing volcanic and sediment rocks forming orebodies containing economically valuable minerals and extensive areas of naturally acidic rocks and soils (Besser *et al*. 2007). (Luedke and Burbank 1999; von Guerard *et al*. 2007). Mineralized relict feature remain from the volcanism, including the Silverton caldera, just north and west of the town of Silverton (Figure 1-2). The ores within the caldera are mainly vein-type deposits with extensive volumes of pyritized rock around the vein zones. The sulfide deposits are largely composed of iron (e.g., pyrite), copper (chalcopyrite), lead, zinc, mercury and arsenic (Luedke and Burbank 1999). Notably, gold and silver are present at variable concentrations.

Figure 1-2.

Figure 1-3

With these and other elements present at economic scales, the region was subject to extensive mining from 1871 until 1991 when the last mine closed (Fig. 1-4). During 120 years of activity, more than 300 large mines and thousands of smaller claims produced silver, lead, gold, zinc, and copper from 18.1 million short tons of ore extracted primarily from hard rock mines burrowed into the rugged mountains (Jones 2007). Many of those mines are now abandoned and continue to leak acid mine drainage to the rivers.

Figure 1-4

Mining Impacts on Water Quality. Along with the veins of mineable metals, the natural geological conditions in the ore bodies create extensive areas of naturally acidic rocks and soils within the upper Animas basin. Acid drainage occurs when either surface or groundwater seepage intersects with the sulfide-rich ores in situ or in the overburden and waste piles left by mining, in an environment with sufficient oxygen to oxidize and dissolve the sulfide minerals. A chain of reducing reactions generate acidic drainage (typically sulfuric acid) with pH between 2 and 5 that is laden with a concentrated mixture of metal ions dissolved from the ores. These typically include some combination of iron, aluminum, zinc, cadmium, copper, lead, arsenic, nickel and other trace metals (Wirt et al. 2007). We refer to the acidic drainage as “acid mine drainage” or AMD even though some acidity is naturally generated.

Acid Mine Drainage (AMD). AMD presents two general areas of concern for water quality in receiving waters: 1) acidity and acid generation; and 2) mobilization of high concentrations of metals in dissolved and colloidal phases. Many metals occur ubiquitously in soils and water in trace amounts and are essential to life. In higher concentrations they can adversely affect human or ecosystem health. EPA, states and tribes have identified concentrations for short or long-term exposure to metals in water or sediment that are protective of human or ecological health. In much of the upper Animas River, concentrations of a number of metals exceed levels of concern for acute and chronic toxicity for aquatic life. These metals include dissolved forms of aluminum, zinc, copper and cadmium as well as colloidal aluminum. The persistence of acid drainage in the headwaters has led to relatively reduced aquatic communities and water that cannot be used for human consumption in most of the Animas River above Silverton (Besser et al. 2001, 2007).

Acid drainage from mines and natural rock formations has been extensively studied in the headwaters of the Animas River at Silverton (watershed area 346 km^2) where the majority of mineralized rock and mining has occurred. Taking a watershed approach, a team of investigators from the U.S. Geological Survey's Abandoned Mines Initiative studied the geological and anthropogenic sources of acid drainage, hydrologic mechanisms and volumes delivered to streams, and the biological impacts of metals in the acidic waters in fine spatial detail. Church *et al.* (2007) summarizes a decade of multidisciplinary research. Patterns and processes leading to acid drainage are very complex and spatially varied within this area reflecting local variations in geology and mineralization, and mining activity (Schemel and Cox 2005; Bovee et al. 2007; Church et al. 2007).

Hardrock mining activity has contributed significantly to the generation of AMD in streams (Church *et al.* 2007). Mining excavations created many miles of underground workings that have significantly altered subsurface hydrology at a hillslope scale. The mining voids collect and provide preferential flow paths for groundwater while the voids provide an ideal environment for oxygen enrichment that triggers the acid-producing reactions in the ore deposits (Fig 1-5).

Figure 1-5

Acidic drainage accumulates to some extent in most mines with significant effluent from some. At active or remediated mines, AMD is pumped out and treated with a pH neutralizing agent such as calcium carbonate ($CaCO^3$) that stimulates the formation of iron and aluminum oxides that precipitate as solids that can then be disposed of (often referred to as sludge). Closed and untreated mines collect water that may leak from the mine entrances or seep slowly via subsurface pathways to streams. More rarely, AMD spills catastrophically with failure of aging and unmaintained infrastructure (BOR 2015). In addition to drainage from inside the mine, excavations also have left large volumes of tailings and mine-waste rock that had been pulverized to remove sulfide ores outside the mines (von Guerard et al. 2007). Mine waste piles at mine and milling sites magnify the surface area exposure of pyrite ores to oxidation and water increasing potential for runoff of AMD.

All three of the main tributaries of the Animas that converge near Silverton are characterized by low to moderate acidity and high concentrations of dissolved metals due to natural processes and mining activities. Cement Creek naturally has the lowest pH as it dissects the Silverton caldera giving it the greatest exposure to sulfide ores. Both upstream and downstream of Cement Creek, the upper Animas River branch is buffered at moderate alkaline pH by the sedimentary bedrock with abundant carbonate and chlorite minerals.

Dissolved-metal concentrations are suppressed when initially acidic waters mix and dilute with inflow from moderately alkaline, well-buffered pH in the Animas River as it flows southward from the headwaters. Increasing pH triggers oxidizing reactions that reduce the solubility of metal ions such as Al^{3+} and Fe^{3+}. As these reactions progress, amorphous iron or aluminum oxyoxides and sulfates precipitate (Schemel *et al.* 2000; Schemel and Cox 2005). In turn, dissolved concentrations of trace metals decreases as they sorb or integrate into the iron and aluminum precipitates (Schemel *et al.* 2007: Wirt *et al.* 2007).

The colloidal solids impart the distinctive staining of the river commonly called "yellowboy", which can be yellow, red, white or black depending on the dominant metals (Schemel *et al.* 2000). Yellow staining is a persistent feature in the Animas River for several kilometers below its confluence with Cement Creek due to the prevalence of iron (Fig. 1-6) (Besser et al. 2007).

Figure 1-6

Eventually the colloids may be lost from the water column to the stream bed (Schemel et *al.* 2000) where the insoluble Al and Fe oxides and similar compounds form coatings on the stream bed (e.g.,Theobald et al., 1963; Chapman et al., 1983; Rampe and Runnells, 1989). A combination of chemical, physical and biological processes promote their long term retention in the streambed (Schemel et al. 2007).

Mining also strongly influenced metals in river sediments. It was common practice through much of the mining era to discharge mill tailing directly into water bodies. By the time mining ended, more than 8.6 million short tons of mill tailings and waste had been discharged directly into the Animas River and its tributaries (Jones 2007). Substantial amounts of the discarded waste has been subsequently transported downstream and dispersed in historical stream deposits headwaters (Church et al. 1997; Vincent and Elliott 2007), while considerable amounts remain in place. Church et al (1997) found bed sediments of the Animas River far downstream of the headwaters to be contaminated with metals that could be traced to the headwaters and its historical mining practices. Early in the 1900's, Durango built a new reservoir and delivery system from the more distant Florida River to create a better source of public water supply and avoid using water from the tailings-laden Animas River (Jones 2007, citing Durango Democrat, August 1-15 and November 18, 1902).

Remediation. For decades, stretches of the Upper Animas River and its tributaries have not supported healthy communities of fish and other aquatic life. Since 1998, Colorado has designated portions of the Animas River downstream from Cement Creek as impaired for certain heavy metals, including lead, iron and aluminum. Colorado had developed numerous water quality cleanup plans under the federal Clean Water Act to address mining contaminants. Numerous projects had been implemented to control "nonpoint sources" of mining waste on public and private lands with funding provided under EPA's nonpoint source control grant program under Section 319 of the Clean Water Act and other public and private sources (BLM 2007, BOR 2016).

The ultimate goal of the USGS AMD research project in the Animas watershed was to better inform remediation activities by identifying those mines that contributed the greatest to AMD pollution and that could be most readily reclaimed (Church et al. 2007; BOR 2015). The State of Colorado Water Quality Control Divison and the U.S. Environmental Protection Agency have also conducted studies to assess impairment and remediation opportunities. The U.S.G.S study determined that the bulk of the metals loading the Animas River was generated from about 80 sites out of 4,500 inventoried in the watershed.

Gold King Mine Release. The Gold King Mine (GKM), located in the Cement Creek basin is one of those mines. In the project remediation plan, the Colorado Divison of Reclamation, Mining and Safety (DRMS) described this mine as one of the worst draining mines in the state of Colorado due to extremely poor water quality and very high outflow rates (see DRMS project summary provided in BOR 2015). Outflow rates have varied considerably over time with most recent estimates varying from 300 to 480 gpm. Using approximately 300 gpm measured in 2006 (BOR 2015), the daily discharge of AMD from the Gold King Mine is approximately 430,000 gallons per day and almost 160 million gallons per year. The mine's effluent had been treated at times in the past but had been largely uncontrolled in the last decade. The EPA and DRMS initiated a more comprehensive treatment project in 2014.

On August 5, 2015, equipment operators were conducting a preliminary site investigation to develop plans for reopening the mine for active remediation. The mine entrance and a drain that had been previously installed was blocked by emplaced fill as well as rock and soil debris that had slipped from the slope above (BOR 2015). As the heavy equipment disturbed the pile at the mine entrance, a small trickle of water grew quickly into a flood that rapidly drained the mine pool collected behind the blockage (Fig 1-7). Over the next 7 hours 3,000,000 gallons of very low pH AMD with high concentrations of dissolved metals drained from the mine into Cement Creek. Adding to the severity of the event, the initial flood of water eroded soil and rock debris from the mine portal and pyritic rock and soil from the adjoining waste-rock dump and swept away the road-embankment fill of several downstream unpaved road stream crossings in its path to Cement Creek (BOR 2015). The flood also entrained sediments and associated metals from the Cement Creek channel.

Figure 1-7

GKM Release Travel Through the Rivers. Although the headwaters of the Animas River routinely receives acid mine drainage from hundreds of mines each day, this blowout event was unique (although not unprecedented). The uncontrolled release of a large volume of AMD within a short period of time traveled rapidly as a plume carrying a large volume of very acidic water contaminated with very high concentrations of metals much farther downriver than has occurred in recent times.

As soon as the plume exited Cement Creek and joined the Animas River, the same geochemical reactions of routinely observed near Silverton began to neutralize the plume's acidity and triggered the geochemical reactions that form iron and aluminum oxides. In this case, the large volume turned the river bright yellow that intensified as it travelled (Fig. 1-8). The plume of mine water subsequently worked its way through 200 km of the Animas River where it joined the San Juan River at Farmington, New Mexico 3 days later. From there the plume continued westward towards Lake Powell 400 km distant. Plume visibility was lost through much of the San Juan due to high pre-existing sediment loads.

Figure 1-8

There was considerable public concern about metals contaminants in the water throughout the river system. The release potentially impacted many communities within the states of Colorado, New Mexico, Utah and Arizona and the tribal reservation lands of the Southern Ute Indian Tribe, the Ute Mountain Ute Tribe and the Navajo Nation (Fig 1-9). Many communities and individual residences obtain their domestic source of water from the river or wells drilled into its adjacent floodplain. Irrigation draws heavily from the Animas and San Juan Rivers in August when the release occurred, especially along the alluvial valleys from Durango CO through Farmington NM. Recreational boating and fishing are popular on the Animas and San Juan Rivers and subsistence fishing is important. The release and the movement of the plume through the system was reported widely in the media as it occurred and public awareness and concerns for water safety both as the plume passed and possible subsequent effects were and remain very high.

Figure 1-9

EPA established a Unified EPA Area Command that coordinated the activities of three EPA Regions that serve the area and state agencies and communities and tribes. Water use for domestic supplies, irrigation, livestock and recreation were curtailed while alternative water sources were provided for a number of days during and after the passage of the plume. The EPA, states and tribes also mobilized monitoring programs to sample for metals contamination in the river water and sediments, irrigation ditches, and wells throughout the Animas and San Juan Rivers. The initial monitoring focused on determining the extent and duration of contamination to inform management decisions. Although the monitoring was largely uncoordinated among organizations, they used similar methods following protocols already in place for various ongoing monitoring programs. Collectively they amassed a significant data record of water and sediment quality during the plume and in the months afterward. These organizations have also continued monitoring since the release to assess longer term effects.

Research Need. There were many concerns regarding the Gold King Mine release and the slug of AMD that it generated as it passed through the 600 km of river potentially affected. Important questions raised by the affected communities include:

- What was the composition and amount of contaminants released from the Gold King Mine?
- Where did the material in the release volume go?
- How was water quality affected?
- What was the potential for water user exposure to adverse levels of metals?
- Does any of the material remain in the river system?
- Will that material be released into the river and will it have delayed impacts?
- Were groundwater drinking water or irrigation sources impacted?
- Have metal concentrations in the water and sediment returned to pre-event levels?

Given the broad geographic scope of the Gold King Mine and dynamic qualities of contamination associated with the plume as it moved, there is a need to integrate the unprecedented volume of data in a comprehensive analysis of the Gold King Mine release and its transport and fate within the river system.

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CHAPTER 2: PROJECT OBJECTIVES, DATA, AND METHODS

Goals and Objectives

The overall goal of this project is to provide a comprehensive assessment of the Gold King Mine release of contaminated mine effluent at its source and to quantify water quality characteristics as it moved through the Animas and San Juan Rivers. Specific objectives were to:

- Quantify the release at the GKM source
- Quantify transport and fate of metals in the Animas and San Juan Rivers
- Characterize potential exposure to metal concentrations as the plume traveled through the system
- Assess the status of metals in water and sediments in the months after the event
- Predict future mobilization of metals that remained in the streambed

Project Area

The project area includes the Gold King Mine site as the source of the release, Cement Creek that initially received the release, the length of the Animas River between its confluence with Cement Creek to its confluence with the San Juan River in Farmington NM, and the San Juan River from its junction with the Animas to Lake Powell. The total river length between Gold King mine and Lake Powell is 550km.

Because this was a release event, the project focuses on the river continuum within this length and does not address general watershed inputs of water or metals except as initializing conditions on water volume or constituent concentrations at the key river junctions. River flow characteristics are obtained from multiple USGS gages distributed throughout the study area, precluding the need for watershed scale modeling to generate streamflow. The project investigates the river interaction with groundwater in the alluvial floodplains adjacent to the river in several segments of the Animas River.

The rivers flows through many different geomorphic settings that influenced the characteristics of the Gold King plume as it traveled and deposited (Fig. 2.1). These would have important influence on the transport and deposition of the Gold King release. The entrance to the Gold King Mine lies at an elevation of 11,400 feet in the San Juan Mountains. The release spilled into Cement Creek at the bottom of the hillslope 70 meters below the entrance from where it traveled rapidly through 12.5 km of a steeper mountain stream before joining the Animas River in the valley where the town of Silverton is located. From there, the river flows southward for approximately 50 km through a steep and narrow canyon carved into the Precambrian basement rocks with morphology characterized by riffles, cascades, and falls. The river abruptly exits the canyon at Baker's Bridge about 30 km north of Durango where it flows into an alluvial valley that contains the river as it flows 130 km before joining the San Juan River. Upon exiting the canyon, the river is heavily braided for several kilometers before establishing a meandering form that persists through Durango. The river is more tightly constrained with a straighter course within the valley walls the rest of the distance to Farmington. Most of the population within the basin lives within or adjacent to this alluvial valley that includes the population centers of Durango, CO and Aztec, Floravista and Farmington, NM and the Southern Ute Indian Tribe reservation.

Figure 2-1

The Animas River joins the San Juan River at Farmington, NM. The San Juan flows through the states of New Mexico and Utah and the tribal lands of the Navajo Nation and Ute Mountain Ute Tribe (Fig 2-2). The river flows westerly towards its junction with the Colorado River within a valley that for most of its length is incised into a series of sedimentary rock formations at various depths. Flow upstream of Farmington is regulated by the Navajo Dam and the valley supports irrigated farming downstream to about Ship Rock NM. The San Juan ultimately flows into Lake Powell created by the Hoover Dam on the Colorado River.

Figure 2-2.

Water Quality Sampling and Methods

The spatial and temporal distribution of sampling of the water and sediments of the Animas and San Juan Rivers by multiple agencies following the spontaneous release of the Gold King Mine effluent was probably unprecedented in the annals of these kind of events. The rivers were sampled intensively at many locations during passage of the plume and in the next several months after it passed. Sampling has continued in the spring and summer of 2016 at lower intensity than in the days after the event.

Almost as soon as the GKM release occurred, the EPA mobilized field crews to begin sampling water quality and river sediments that would be analyzed for metals. Crews arrived at Cement Creek where the spill occurred within 5 hours and began sampling in the headwaters. Sampling was rapidly expanded to rest of the Animas and San Juan Rivers (Fig. 2-2). EPA Regions 8, 6 and 9 worked in conjunction with the Colorado Department of Public Health and Environment (CDPHE), and the Utah Department of Environmental Quality (UDEQ) collected water samples as the plume passed through upper Animas and lower San Juan Rivers, respectively.

Field crews sampled surface waters in the Animas and San Juan Rivers as well as groundwater in public and private wells in Colorado and New Mexico. The New Mexico Environment Department (NMED) sampled water within the lower Animas and upper San Juan Rivers. Working with the Navajo Nation (NNEPA), EPA coordinated sampling activities on the San Juan River and Lake Powell. The Southern Ute Indian Tribe (SUIT) collected samples from the middle Animas River on tribal lands as did the Ute Mountain Utes in the middle San Juan River. The US Geological Survey collected samples at stream gages. We refer to these data contributors collectively as "data providers. Analyses of the Gold King Mine release rely solely on data collected by these organizations. The general distribution of sampling locations is shown in Fig. 2.2.

Table 2-1:

Data collection was focused on the sampling water and sediments for their concentration of the priority Metal/Cyanide Analyte List (TAL) of 23 metals plus molybedenum. Samples collected for analyzing the TAL metals follow EPA Procedure 200.7 or 200.8 (US EPA 2001; US EPA 1994), both of which have the same field sample preparation requirements.)

Data was obtained from publicly accessible websites sponsored by the data providers listed in Table 2.1 as it became available. Detailed information about data sources, sites, methods and quality assurance and website links are provided in Appendix A. The EPA website also provides a number of links to information about the release, relevant reports, and data: https://www.epa.gov/goldkingmine

Additional background information on data and sources available in Appendix A is summarized in Table 2-2. These include links to data sources, information about testing methods used by each provider, sampling locations and identifiers, and quality assurance documentation links: https://www.epa.gov/goldkingmine.

Data providers collected samples and processed them using similar laboratory procedures following quality assurance documented procedures and protocols. Many of the data providers also submit data for public access to EPA's STORET database where some of the data was obtained.

Table 2-2

Field Methods. Water and sediment sampling began almost as soon as the GKM release and has been ongoing on varying schedules since. EPA field crews and other data providers primarily collect water samples by grab sampling as illustrated in Fig. 2-3. A sample bottle is dipped into the stream as far towards the middle of the stream as possible. Two samples are collected, one of which is filtered in the field and later processed for dissolved metals and one is not filtered and later processed for total metals. Some data providers do not conduct laboratory analysis for all metals (Table 2.3).

Figure 2-3. Photo

Table 2-3. General overview of metals tested.

Animas River sampling locations are highlighted by data provide in Fig. 2-4 and for the San Juan River in Fig. 2-5.

The USGS collected some depth integrated samples at gage sites during passage of the GKM plume. Depth integrated techniques provide a composited sample collected across the entire width of the channel. There can be significant variability in the concentrations of suspended materials from channel edge to center and depth integration often gives a better representation of the material in transport unless there is little flow variation such as in a highly turbulent stream. However, this technique requires specialized equipment and either safe wading conditions or over-stream access via bridge or cableway and requires considerably more time to collect a sample. With these three exceptions, all water samples were collected by grab sampling, probably near the channel margins of the larger rivers..

To determine of the dissolved elements, the sample is filtered through a 0.45 μm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. The filtrate is then acidified to pH < 2 with (1+1) HNO_3 immediately following filtration in the field. For determining total recoverable elements, aqueous samples are **not** filtered, but acidified with about 3 ml of (1+1) HNO_3 to pH <2. Acid preservation may be done at the time of collection or in the laboratory within 2 weeks of collection. A field blank is also prepared for later analysis using the same conditions (i.e., container, filtration and preservation) as used in sample collection. Data providers routinely collected duplicate samples.

Sediment samples are collected by shoveling the top layer of sediment to a depth typically less than 5 cm. The sampler may composite sediment from several locations at the sampling site. Because much of the initial sampling for GKM was to assess potential risk to contaminants to guide management actions, EPA field samplers preferentially selected obvious deposits of GKM material. For research purposes, this sampling bias could influence comparisons with pre-event sediment samples. Sediment samples require no field preparation or preservation prior to analysis other than storage at 4°C and there is no established holding time limitation for solid samples. (US EPA 2001).

Laboratory Procedure for Metals and Metalloids. Most samples included in this analysis were analyzed by contract laboratories, with the exception of the first samples from August 5 that were processed in Region 8 laboratories. Contractors for EPA and other data providers analyzed for the TAL metals using EPA methods 200.7 and 200.8. Table 2-4 lists provides methods and technology by metal analyte. The complete list of methods used by individual data providers is compared in Appendix A Table A.3. Note that USGS laboratory methods for metals and metalloids include EPA 200.7 and 200.8 but USGS also applies several other protocols and technologies for these metals.

Table 2-4. Testing methods

Samples were immediately shipped to the laboratory. The laboratories check pH upon receiving the sample, and if pH > 2, acid is added and the sample is held an additional 24-hours. The sample is also checked for turbidity; if turbidity > 1 ntu than the sample is digested using EPA method 3050B or 6010A). Contractors report that all samples collected during the plume release were digested.

The sample digest is then placed on the analysis instrument with batch QC samples including method blanks, spikes, and laboratory control samples. Sample data and associated QC results are loaded directly from the instruments into the Lab Information Management System. The results undergo several internal quality control checks before the data report is released.

Field crews for all data providers routinely collect supporting parameters in the field such as pH, specific conductance, and temperature (Table 2-5). States and some tribal data providers also had samples analyzed for additional analytes including hardness, sulfate.

Table 2-5. Field parameters

Sondes were deployed in 6 locations (5 in the lower Animas River and 1 in the upper San Juan River) during the passage of the GKM plume (Fig 2-4; Table 2-6). A sonde is a water quality monitoring instrument that may be stationary or move up and down in the water that typically measures multiple water quality attributes and continuously records various water quality attributes and continuously records them electronically. Each sonde had 6 onboard probes, which varied by data provider. All recorded pH, specific conductance, temperature, and parameters that measure oxygen saturation (ODO Saturated and ODO Concentration). The three New Mexico Environment Department (NMED) instruments measured turbidity and the 3 SUIT instruments measured Total Dissolved Solids (TDS). .

Table 2-6. Sonde Parameters

Figure 2-4 Sonde location map

Geochemically relevant parameters that could assist with equilibrium calculations related to acid mine drainage were highly desirable but were sparse or absent in the available data. Measurement of acidity in the water phase with a heated pre-oxidation step followed by titration with a base (EPA Method 305.1) would allow speciation of dissolved Fe^{2+}, Fe^{3+}, Al^{3+} and Mn^{2+} that would improve understanding of metal mobility and potential for precipitation or dissolution of ferric and ferrous minerals. A limited amount of sulfate measurements were available. Sulfate ($SO_4^{=}$) allows calculation of ionic strength, activity coefficients and complexation. Selective extraction of sediments, perhaps including oxalate and/or dithionite extractions, might aid interpretation of solids formed by reactions of AMD in the environment. These were not measured during the passage of the GKM but would have enhanced geochemical interpretations.

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Sampling Locations. Collectively, the data providers sampled water and sediment quality at numerous locations covering the entire river length within the Animas and San Juan Rivers and Lake Powell at numerous locations. EPA and the states have sampled both water and sediment at some of these sites while tribal partners have done less sediment sampling (Table 2-2).

River sampling has been the primary focus for GKM monitoring before and since the GKM release. There are about 180 river locations that have been sampled repeatedly or once. Sampling locations for surface water and sediment are shown by organization for the Animas River in Fig. 2-5 and the San Juan River in Fig. 2-6. Sampling sites are distributed throughout the river system but are clustered within the most heavily populated areas of Durango, and Farmington. There are long distances between sites in river segments that are very remote or with difficult access, including the canyon reaches of the upper Animas.

Figure 2-5 Animas River sampling sites

Figure 2-6 San Juan River sampling sites.

A number of additional sites were sampled during or immediately following the plume for a brief period as part of agency efforts to understand and manage public exposure to contaminants in the water or sediments. Short-term water sampling was conducted at 16 water supply intakes and off channel ponds and sediment was sampling in 68 irrigation ditches. Many of the irrigation sites were measured once or a few times until it was determined the water was safe to use. Some water supply intakes are routinely sampled. Each data provider included the geographic coordinates (latitude, longitude) of sampling sites. A complete integrated list of the 251 sampling sites is provided in Appendix A..

Monitoring has continued since the GKM plume passed. Longer term sampling has focused on a more limited set of river sites to determine whether water and sediment metal concentrations have returned to pre-event conditions. Many of these locations are sites of ongoing or historic monitoring programs implemented by the data providers for various objectives. These sites include several in the headwaters of the Animas that were initially part of the USGS AMD project (Church *et al*. 2007) and continue to be part of remediation studies. Site information including assigned distance from the Gold King mine are provided in Table 2-7 highlights the sites where many of the project analyses were focused due to availability of data.

Table 2-7. Site distance

Streamflow. Streamflow measurement is essential to study of the passage of the release from the Gold King Mine through the river system. There are 13 USGS stream gages located in the Animas and San Juan Rivers that were used to inform these analyses (Table 2-8). Locations of the USGS gages are shown in Fig. 2-7. There is a USGS gage located in Cement Creek where the spill occurred that could be used to determine the spill volume. Data from the 10-day period following the spill were used to characterize the plume transport of metals during the plume. Long term gage records were used to simulate potential mobilization of metals during storms and spring snowmelt.

Table 2-8.

Figure 2-7.

Sampling Schedule. Initially, sampling was oriented to support risk assessment within the river system. Once the plume passed, sampling became more oriented to monitoring for return to pre-plume water quality and potential secondary impacts from metals that may have been deposited within the river system. Sampling frequency reflected that transition. To meet project objectives, we sought metals data collected in the Animas and San Juan Rivers in three distinct time periods.

Plume Period. The first period includes the time from the release event to the completion of the plume's movement through the rivers. It took nine days for the plume to travel the distance from its start at Gold King to Lake Powell, but only a few days to pass any specific location. During the GKM plume, sampling frequency was the discretion of each data provider subject to objectives, availability of personnel and the distances involved in visiting the sites they chose to sample. Timing of samples during plume movement was critical, as the bulk of material moved past each location fairly quickly and concentrations rose and fell significantly within a narrow time window. Some sites were visited daily while others were visited once or a few times. A select group of sites were sampled multiple times at relatively short intervals as field crews anticipated the arrival of the peak of the plume. A few sites located in close proximity to one another were sampled by different data providers whose combined visits collectively intensified sampling during the plume. This project largely relies on sites that were measured multiple times, a number of which have become long-term monitoring sites.

Post-plume Period. The second phase considers the return of the river to pre-event conditions. This period began as soon as the plume passed and continues through the fall and winter months of 2015-2016 when flows typically reach their lowest point. This includes late fall storms that may be captured in the data record. Sampling emphasis during this period was on monitoring water quality and sediment for trends and recovery at a selected group of sites, with sampling daily to weekly. Sampling during the low flow winter months was curtailed in the headwaters of the Animas and throughout most of the system. Most data providers resumed sampling in the spring at 1 to 2 samples per week. There are plans to more intensively monitor spring snowmelt when deposited materials from the GKM plume would most likely be entrained into the water column and transported downriver, potentially creating a secondary flush of metal contaminants. This project included data collected through June 2016.

Pre-Event or Historic Data. We have also assembled historic metals data collected prior to the GKM plume in order to evaluate post-event trends in water quality. Metals data was available at a number of the same locations in the two rivers from the same data providers (Table 2-1).

Monitoring and research occurring prior to the GKM Release Incident have identified pre-existing impairments or established baseline conditions of water and sediment quality, and biological communities in this watershed (e.g. Church et al. 2007). These data were primarily available from EPA's STORET database where data providers deposit data for public access. These data were more variable in methods and analytes as they had been generated for a variety of purpose over a long period of time.

USGS compiled all the agency's data collected in the geographic area encompassing the Animas and San Juan watersheds over 60+ years and made it available referencing it as the Gold King (USGS Gold King Mine Release Database; see Appendix for link). Much of that data was not pertinent to this project objectives, but it provided 300 + metals samples from water quality and sediment that were helpful for trend comparisons.

Consolidated Integrated Data

This project utilizes publicly available data gathered from the data providers listed in Table 2.1. When completed, we obtained more than 1,400 samples collected since the Gold King release. Data were obtained from providers posted on websites as either Excel or Access electronic files or occasionally in paper format. All varied in naming conventions, file content and organization but all contained key information regarding sampling, and laboratory analysis. The files contain sampling location and time, metal concentration, usually both dissolved and total fractions. They may have additional laboratory analytes and field collected parameters. They contain reference to laboratory testing methods for each analyte, and quality assurance documentation from the laboratory tests.

The project approach was use to use as much of the data as possible to provide as robust analysis of the GKM release and its fate and transport in the system. We compiled quality assurance documentation and concluded that the critical metals data was almost uniformly collected and processed using the same methods. (Appendix A) allowing us to integrate data from multiple providers.

We synthesized the available water quality and sediment data collected by multiple organizations and compiled them into integrated data sets. We filtered for parameters of interest. These included sampling organization, sampling time stamps and location information including station name and identifiers and latitude and longitude. The integrated data sets can be traced to original data through these identifiers. Analytes included the 23 TAL metals + molybedenum, sulfate and hardness when available, and field parameters including specific conductance, pH, turbidity and suspended sediment concentration. We created files for dissolved and total metals in surface water and sediments for the GKM event-related data and a separate set of files for historic data.

Many of the data sets often had a number of sites within the watersheds including tributaries where monitoring is conducted for various purposes. We concentrated on the sites located on the Animas and San Juan Rivers.

Laboratory quality assurance information is included in the available data sets. We extracted the detection status of the sample. When below detection limit, we assigned a value of one half the limit. The file also allows the sample to be excluded if desired. Original data files were always available to refer back to sample qualifiers added during laboratory analysis. Concentrations were adjusted to the same units of measure. We generally use either ug/L or mg/L for water concentrations and mg/kg for sediment concentration.

We added an important variable used throughout the analysis to integrate data results. Distance from the Gold King Mine was the main organizing and identification parameter that integrates the data in our analyses. Each site was assigned a distance from the plume source starting at the Gold King Mine entrance. Distance of each site from this starting locations was established using the line tool in EPA's measurement tool on the EPA Gold King mine website [1]. Managers of the tool had previously traced the river path placing a marker every 5 miles.

We note that establishing the distance of locations along a river course in GIS systems requires subjective decisions by the analyst; no two analysts are likely to produce the exactly the same distance. The distances established for sites in this project were based on the EPA website distances. This choice was to remain consistent with EPA data, which is the largest portion of data used in the project. The National Hydrography Dataset Plus (NHD+) and NHD High Resolution spatial data also performs river distancing at various levels of resolution. In a test segment 12 km in length, the EPA tool distance was within -0.5% the distance of National Hydrography Dataset High Resolution (NHD high resolution length for the segment. The cumulative distance from Gold King Mine to Mexican

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[1] The measuring tool used in the study, is part of the interactive sampling sites map available from EPA's "Emergency Response to August 2015 Release from Gold King Mine" webpage (https://www.epa.gov/goldkingmine/emergency-response-monitoring-data-gold-king-mine-incident). To use the tool, expand the Measurement menu on the left side of the map, and select the ruler icon.

Hat, Utah determined from NHD high resolution is 426.4 km and the EPA tool-based distance is 421.3 km (-1.2%).

Data providers supplied the latitude and longitude of each site, presumably established with a GPS device in the field. Our project GIS analyst added each site into the EPA established mile marking system and measured its distance to the nearest established mile marker using a similar tracing technique. Distances should be viewed as approximate. The term "distance from GKM source" used in this report refer to each site's distance from the Gold King Mine source. Table in Appendix A provides the distance from source for all sites in the compiled database. We note that the critical first leg of the GKM path from the mine entrance to the Cement Creek gage is listed by 12.5 km using the EPA tool. This site appears to actually be 11.6 km according to NHD High Resolution. For consistency however, the distance assigned to the gage is 12.5 km. This discrepancy is important in later estimates of travel time but not for general organization of study results.

Data Quality and Uncertainties

Whenever merging data from multiple data sources there is the potential for unexplained sources of variation due to differences in sampling protocols or testing methods. Critical data collected in response to the Gold King Mine release was obtained and processed using similar protocols (the EPA 200.7 and 200.8). Nevertheless, specific decisions regarding field and laboratory procedures employed by each of the data providers, including biases in sampling during the event, likely introduced unexplained variations in data when merged.

Note that there is generally a great deal more variability in methods, analytes, and media within the historic data sets. Similarly, historic USGS data was developed with many different methods due to the myriad of project objectives that have spawned data collection over decades.

Establishing comparability of samples was challenging. We were able to match a few samples collected by different data providers at the same of nearby locations at similar times during plume passage. They generally matched well and were within the same level of variability as duplicate samples. Occasionally there were marked differences which will be discussed where appropriate. We are very comfortable that the combined datasets provide an internally consistent data set at a scale of variability needed for robust analysis of plume movement and characteristics. Small variability among samples was dwarfed by the large concentrations of metals as the plume passed.

These uncertainties all manifest much more in post-event analysis of water quality trends. Metals concentrations are much lower during this period and often at or below method detection limits for many of the metals. Statistical comparisons of data collected over many years by different organizations for various purposes are subject to biases that may exist due to sampling or laboratory procedures.

The distinction between dissolved and solid phases of metals is an important basis for interpretation of Gold King Mine release effects. Metal colloids are likely to span a range of particle sizes from nearly nanoparticle size (.010 microns) to as large as (40 microns) (silt-size). The filtering of samples at 0.45 micron mesh is not a natural (or effective) break for distinguishing dissolved from particulate fractions (Church et al. 1996). Earlier USGS studies used ultrafiltration techniques to improve isolation of truly small dissolved metals (Church *et al*. 1997). Data reported as dissolved in this analysis may include a portion of colloidal particles that were able to pass through the filter.

The distinction between dissolved and colloidal fractions of metals is important to many of the hydrodynamic, geochemical, and biological analyses applied in this project, including evaluation of concentrations relative to water quality criteria as an indicator of potential adverse effects. Field sampled metals data ware reported as total (unfiltered) and dissolved (typically filtered with 0.45 micron mesh). We subtract dissolved from total to obtain the solid phase we refer to as colloidal/particulate. We will routinely use the term colloidal/particulate to refer to the difference between these measures and at various phases.

Overview of Research Approach

The focus of this project was to quantify and track the metals and acidity released from the Gold King Mine blowout as it travelled through the river system and to evaluate the attenuation and latter release of metals through deposition and resuspension processes. A basic premise of the project was that transport and storage of the released metals would depend on hydrodynamic and geochemical processes during movement of the slug of contaminants with the flow of the river. Plume travel and composition was dynamic in space and time, both as the plume moved and for some period after it passed.

Two perspectives of metals transport will be maintained throughout the analysis. The concentration of metals in the water and sediments is prominently evaluated because it is important for establishing potential exposure to adverse levels of the metals carried in the GKM plume. Potential health or ecosystem effects result from exposure for some length of time to various concentrations of a contaminant. Determining the mass of metals transported or deposited allows us to track the Gold King Mine release volume within the system and to distinguish it from pre-existing and background constituents in a river system known to be contaminated from mining activities for over a century. Mass is determined by multiplying the concentration (expressed as volume per unit of water or sediment) by the relevant volume of flow (expressed as liters) in this study.

We apply a multi-faceted analysis of factors that affect metals concentrations and mass from source through the river system using a combination of data analysis supported by modeling. Data analysis uses the considerable amount of monitoring data generated during and after the Gold King release in the Animas and San Juan Rivers. Empirical analysis entails quantification of the status and statistical analysis of trends as well as building empirical models of metals transport during the plume and on an annual basis. Process-based analytical soft-ware assisted models are deployed to assist understanding of the dynamics of metals transport and transformation processes within those same time frames. In this chapter we describe available data and present an overarching map of the research approach to the multifaceted analysis empirical and modeling study.

We combine empirical analysis of metals data collected by the data providers during, before and after the event and process-based computational analysis enabled by software analytical models. Here we provide a general overview of the empirical and modeling approaches. Specific methods and application to the defined problem will be described with each analysis. Model parameterization and calibration are provided in Appendices.

We reconstructed and characterized the plume using the water sampling data and a water quality model. **WASP (Water Analysis Simulation Program) version 7.52** is a water quality simulation program that simulates movement of contaminants in the river system through the length of affected river. WASP enabled analysis of the pattern and timing of plume movement. This could not be reliably determined or visualized from the monitoring data alone. WASP was calibrated to flow at multiple USGS gages and to the empirical reconstruction of concentration and mass as selected locations along the river. These two models working in tandem reproduce water concentrations and metals mass movement. WASP is also used to address likely remobilization of deposited material in subsequent high flow in the snowmelt period.

Geochemical reactions and transformations are important processes controlling the characteristics and fate of metals released from Gold King Mine as the plume travelled through the river system. Geochemical calculations are informed by observed water chemistry and assisted by the Geochemist's Workbench® software (Bethke 1998) for solving the stoichiometry of equilibrium chemistry. Geochemical analysis focused on neutralization of acidity and the subsequent transformation of dissolved metals to colloidal precipitates. In reconstructing the plume, the empirical and modeled mass transfer of metals was integrated with geochemical analysis. Lack of geochemically-relevant data limited the scope of geochemical analysis.

Questions arise as to whether wells drilled into the alluvium adjacent to the Animas or San Juan Rivers could have drawn in GKM contaminated water given that water can move from the river into sediments. Potential groundwater exchange between the river and wells was examined using groundwater modeling in several locations in the Animas River to explore floodplain scale and local level interactions between wells and the Animas River. The regional groundwater model GFLOW and local 3-D model MODFLOW were applied (Table 2-9).

Temporal and spatial trends in water and sediment quality are explored with empirical analysis of data collected before, during, and after the plume. Metals concentration data have been collected on an irregular basis at various locations in the Animas and San Juan Rivers, allowing comparison of water chemistry in the river and sediments after passage of the Gold King plume relative to pre-event to assess if and when the system returns to its normal contaminated state. Wherever possible, findings from software models are calibrated and compared to observed data and synthesized with empirical analyses.

Potential impacts on water users were assessed by comparing the plume water concentrations and post-event sediment concentrations to relevant federal, state and tribal water quality criteria. Potential dietary impacts from consumption of fish exposed to metals are also assessed by applying a bioaccumulation to the time trend of metals concentrations in the plume and as well as annual patterns of concentration to characterize baseline body burdens at several locations within the Animas River. EPA's BASS (Bioaccumulation and Aquatic System Simulator) model **BASS** is a fish bioaccumulation model that estimates the population and bioaccumulation dynamics of age-structured fish assemblages. Chemicals and metals can be accumulated from food or breathed in through the gills. Even though the duration of the plume was short, fish can rapidly assimilate metals. Did the acidity and metals cause short or longer term effects on fish?

Methods of analysis will be described as they are introduced. Models and their calibration are also more fully described in Appendices.

Table 2-9. Model list

The following chapters organize results and analysis:

Chapter 3: Mass and volume in the Gold King Release

Chapter 4: Characteristics and processes of the Gold King plume as it passed through the rivers

Chapter 5: Water quality characteristics as the Gold King plume travelled

Chapter 6: Mass transport and deposition during travel of the Gold King plume

Chapter 7: Potential exposure to metals contaminant during the Gold King plume

Chapter 8: Post-Event water quality: water and sediments in the 11 months following the event

Chapter 9: Potential groundwater effects from the plume

CHAPTER 3: GOLD KING MINE RELEASE VOLUME AND CONSTITUENTS

This chapter addresses the events at the Gold King Mine and quantifies the amount of water and metals in dissolved and colloidal/particulate form that were released from the mine and generated by erosion as the spill moved through from the mine through Cement Creek. We determine what was released from the mine and the volumes and mass of metals delivered to the Animas River from Cement Creek.

The Release Event

The Gold King Mine is located in the northern portion of the Silverton caldera within the Cement Creek watershed. Economic production in Gold King began in 1886 and ended in 1923 (BOR 2015). The mine has a complex series of vertical and horizontal shafts that extend roughly 2.4 kilometers (1.5 miles) horizontally and about 210 meters (700 feet) vertically within the mountain. The release was from the mine entrance (adit) at level 7 at elevation 3475 meters above sea level (11,400 feet). The Gold King Mine portal is situated on a steep slope composed primarily of mine waste about 70 meters above Cement Creek (Fig. 3-1).

Figure 3-1

The groundwater regime in the Gold King area, upper Cement Creek, and the Sunnyside Basin is dominated by interaction of extensive underground mine workings and a very complex system of fractures related to the various volcanic flows, tuffs, breccias and faults (BOR 2015). Gold King mine voids interconnect within the mountain with other nearby mines including the Sunnyside, Red Bonita, Mogul and Grand Mogul located at higher and lower elevations. All of these mines are connected to and partially deeply drained by the American Tunnel located at the lowest elevation on the mountain.

Gold King Mine collects water and delivers it to the North Fork of Cement Creek via subsurface and overland drainage at a flow rate that has varied over time (BOR 2015). Flow from Gold King substantially increased when bulkheads were installed in the American Tunnel in 1996. The bulkheads blocked the flow from the Sunnyside Mine as planned but raised regional groundwater and increased discharge at other mines, including Gold King (BOR 2015). Reports of Gold King outflow in more recent years has varied from 285 to the most recent estimate of 480 gpm. At the later rate, 700,000 gallons of AMD are leaked to the north fork of Cement Creek each day at a rate of 1 cfs providing a substantial portion of the streamflow in the mainstem of Cement Creek during low flow. A number of other mines also leak AMD to Cement Creek.

The process of remediating Gold King has been ongoing for several years as a collaborative effort between CODRMS and the EPA with consultation with BOR and others. Preliminary excavations to determine mine conditions within the sealed mine were conducted in 2014 to assess the ongoing adverse water quality impacts caused by mine discharges and the potential for a catastrophic release.

Remediation work was completed on the nearby Red and Bonita mines in early August 2015, from where the contractor crews and equipment moved to Gold King to conduct preliminary investigations to prepare for a multiagency onsite planning meeting scheduled for August 14. While the EPA team was excavating above the main Gold King Mine adit on August 5, the lower portion of the bedrock crumbled and pressurized water from greater than expected hydraulic head behind the blockage began leaking from the mine adit (EPA 2016) (Fig. 3-2)

Figure 3-2.

The small leak quickly turned into a full breach that rapidly drained the mine pool and rushed directly downslope to Cement Creek. Adding to the severity of the release, the initial flood of water eroded soil and rock debris from the mine portal, and a significant volume from the large waste pile outside the mine entrance where processed ore and tailings that had been dumped during almost 40 years of mining operations. The rushing water also swept away the fill of several unpaved road stream crossings in its path (BOR 2015). The flood entrained sediments and associated metals from the Cement Creek channel. See BOR 2015 for a more complete discussion of the mine history and the blowout event.

We consider the release event to include both what came from within the mine, and what was entrained between the mine entrance and the Animas River as the flood travelled into and through Cement Creek. The first step in assessing the Gold King release, was to quantify the volume and content of the acid water spilled from the mine. The second step was determine the volume and content of additional materials entrained outside the mine and as it travelled through Cement Creek before it entered the Animas River.

There are 3 USGS stream gages located in the Upper Animas River that allow quantification of the volume of water released from the Gold King Mine. USGS gage 9358550 that is located in Cement Creek is 12.5 km downstream from the mine at the confluence with the Animas River directly measured the additional water from the mine as it flowed past.

Two gages in the Animas River that bracket the town of Silverton monitor flow immediately above the Cement Creek confluence (09358000) unaffected by the release and 3.8 km downstream from Cement Creek (09359020). These gages provide a reference for flow conditions during the release. The gages record water and streamflow in 15-minute intervals.

Hydrology in Cement Creek During the GKM Release

At the time of the release, streamflow in the Animas and its tributaries was receding after rains several days earlier. Immediately prior to the release, Cement Creek contributed 20% additional flow to the Animas at their confluence (Fig. 3-3)

Figure 3-3

The mine ruptured at approximately 10:45 and was in full drainage mode by 10:55 based on an time stamped videos taken by the onsite crew. The release first arrived at the Cement Creek gage in the 12:45 time period with a 5-fold increase in flow from 0.736 to 3.40 m^3/s within a 15-minute period (Fig. 3-4).

Figure 3- 4

The arrival of the plume at the gage was readily apparent. Determining the end of the release was less clear as flow tapered off slowly after 14:00 hrs. To investigate whether the release extended further we compared the unit area discharge in Cement Creek to the upper Animas River gage ($m^3/s/km^2$) as a reference for Cement Creek. The relative relationship indicated by the ratio of unit area discharge had been quite steady prior to the release as evident by the line fit to the pre-event data (Fig. 3-5). Return to that relationship after the Gold King plume passed may not have occurred until near midnight or possibly as late as 6:00 the next day. However, close examination of the flow records at each site suggests other factors such as diurnal fluctuation may also have influenced the hydrographs at each gage individually.

Figure 3-5

The peak flow observed as the slug of water passed the gage was similar to that observed on a moderate day of snowmelt runoff in Cement Creek (Fig. 3-6). Based on the cross-section and velocity characteristics relative to gage height measured at each USGS gage, water level increased from a low flow height of approximately 0.3 m to about 0.5 m. This moderate stage suggests that the flood probably remained within the banks of the active channel. Based on gage statistics, the velocity of the peak was in a range of 1.40 to a maximum of 1.71 m/s representing the maximum observations in the gaging record.

Figure 3-6

The upper value agrees well with the observed travel time of the plume. The first photograph at the mine adit as water was flowing from the mine was time stamped 10:55 (BOR 2015, or video EPA GKM website.) The first pulse of water traveled 11,640 meters to the gage arriving within the 15-minute window between 12:31 to 12:45. The time of 96 to 110 minutes to travel the distance suggests a velocity between 1.75 and 2.0 meters/second. This is close to but higher than suggested by the gage statistics. Uncertainty in the calculations arise from inaccuracies in the distance measurements and the range of variability in the gage velocity measurements. Generally, however, there was good consistency between the gage estimate and the actual travel time.

Metals Released From the Mine

We estimate the mass of metals released is determined from the concentration of metals in the mine pool and the volume of water released.

Fig 3-7 Photo inside Gold King

GKM Volume from the Mine. The Gold King release volume was assumed to equal the volume of flow in excess of baseflow at the USGS gage from 12:45 to 18:30. Baseflow was taken as the flow at 12:30 and was receded slightly during the time period following the pattern at the Animas upstream gage. The GKM volume was computed as the instantaneous flow rate expressed in m/s and multiplied by 900 for each 15-minute period, then summed from 12:45 to 18:30. The estimated baseflow was subtracted from the observed streamflow in each 15-minute period, interpolated as the midpoint between flow measurements.

From 12:45 to 18:30 close to 3 million gallons (11.33 million liters) of flow volume in excess of baseflow flowed past the Cement Creek gage. This computation concurs with USGS estimates that the effective end of the mine pool volume occurred at 18:30 at this gage with a release of 11,333,000 liters (3,000,000 gallons). The gage records show that the slug of water drained from Gold King passed within about 6 hours but the bulk of the water moved through in 2 hours.

Metals Concentrations. There are no pre-event measurements of the metals within Gold King as the entrance was sealed. There were 4 samples collected from the mine effluent over a six-week period after the release that were used to estimate pre-event metals concentrations. It was expected that the mine pool chemistry would vary after the release as equilibrium of the pool re-established, but that chemistry return to a composition similar to what it was before the mine was unsealed.

Four samples were collected from the mine but only the August 15 sample collected by EPAR8 (EPA Region 8) had complete data for all 24 metals in dissolved and total fractions. Colorado Department of

Public Health and Environment (CDPHE) samples collected on August 7 and August 11 did not report concentrations for several metals. The September 21 sample did not report dissolved metals. Trends in metals concentrations in the mine effluent focus on the commonly measured analytes. Mine water data are provided in Table 3-1.

Table 3-1.

There were trends in the total concentrations in the effluent during the seven weeks represented in the samples. Many of the metals declined rapidly from initially high concentrations observed 2 days after the release (Fig 3-8). Relatively little change in concentrations was observed after the August 15 sample. Calcium (not shown) and beryllium continued to increase through the entire period.

Figure 3-8

Along with a general decrease in metal concentrations in the first 10 days after the release, the proportion in dissolved form increased during this period. Metals were generally colloidal soon after the release but most trended towards dissolved by August 15, suggesting that pH was decreasing. An August 15 the pH in the mine was 2.93 (Fig 3-9). Trends in concentrations and the dissolved/total ratio suggests that the mine pool reached an equilibrium by August 15, although it may not have been the same equilibrium as existed prior to the release.

Figure 3-9

The average of the 3 samples collected after the release and the selected concentrations are shown in (Fig. 3-10). The August 15 sample was selected as the primary basis for assigning metals concentrations to the effluent with three exceptions. Copper and zinc appeared to be anomalously low on August 15 and the higher values on September 21 were used. Beryllium continued to increase through the period so the final sample was used. It is possible that none of the post-event samples represents the mine pool when it was sealed. The only sample that may have represented the mine effluent that was actually collected during the plume was taken from Cement Creek far downstream at 16:00 hours, and well after much of the plume had passed. The dissolved constituents in that sample minus estimated background stream concentrations are shown with the other estimates in Figure 3-10. Dissolved concentrations observed in Cement Creek were generally similar to the post event mine samples. Once in the effluent left the mine, chemical reactions within the stream were likely to have increased dissolved metals and several were significantly higher (aluminum, lead, nickel copper) and several were significantly lower (arsenic, iron, manganese). Based on the stability of the mine effluent by August 15, that sample was the primary selected value to represent each metal in the effluent.

Figure 3-10

Metals mass in the mine pool was calculated by multiplying the volume of effluent (11.33 million liters) by the concentrations of the metals and other constituents. A total of 2,900 kg of dissolved TAL metals excluding the major cations were released from the Gold King Mine, most of which was iron and aluminum. The higher loadings for trace elements included Zn (306 kg) and Cu (79 kg). The rest of the trace metals totaled 5 kg; the mass of lead and arsenic were each approximately 0.5 kg. There was no mercury released from the Gold King Mine.

The mine effluent also contained sulfate $SO_4^{=}$ (18,000 kg), and the major cations (Ca, K, Mg, Na, 4,600 kg). Acidity load was calculated to be 7600 to 8100 kg $CaCO_3$, with this uncertainty reflecting not knowing the valence state of Fe. (Fig 3-11).

Figure 3-11.

Metals Released to the Animas River

Sudden release of the pressurized water sent an erosive flood of water to the North Fork of Cement Creek. Crews captured the event on video, with some stills taken from it shown in Fig 3-12. The release cascaded downslope to Cement Creek, excavating a portion of the waste pile. Substantial amounts of mining waste and soluble salt minerals were entrained into and vigorously washed in the acid for two hours as it traveled downstream before joining the Animas River.

Figure 3-12.

We must consider the erosion once the mine pool left the mine entrance to determine the full measure of metals mass generated from the Gold King Mine release. Outside the mine entrance, there was considerable opportunity for the acidic spill to entrain additional metals. Most prominent was a large waste-rock dump outside the mine entrance. An historical photograph of the operation Gold King Mine at level 7 prior to its closure shows the significant size of the pile that had amassed over 40 years (Fig. 3-13). Mine waste piles are often very concentrated in metals as the residual of ore processing. Depending on the mineralogy, desorption of metals from the ores and dissolution of salts would have increased the dissolved metals depending on pH (Smith 1999, Nordstrom 2011).

Figure 3-13

The flow peak arrived at the USGS gage 12.5 km downstream from the mine at 12:45. The first water sample was collected from Cement Creek at 16:00, well past the peak and probably after the bulk of the mass had passed (Fig 3-4). Even this late in the plume, the summed concentrations of the 24 TAL metals was 12,200 mg/L, a large increase relative to what was observed in the effluent (658 mg/L). Most of the increase was in colloidal/particulates. We assume that the peak concentrations must have been much higher at the peak based on the hydrograph.

We use different techniques to reconstruct the plume and estimate the peak in Cement Creek for the colloidal/particulate fraction which were entrained by physical erosion processes and probably behaved similarly to suspended sediment, and the dissolved fraction which would be reflect mixing of the effluent in stream water. Dissolved metals could have also been augmented through chemical dissolution or desorption from ore and soil particles in the turbulent flow of highly acidic water. For both fractions, the rise and fall of concentrations will follow streamflow and all metals estimates reference from the 16:00 hour sample.

Colloidal/Particulate Metals Plume Reconstruction.

The plume began abruptly at 12:45. Peak metals concentrations were assumed to have occurred at the same time as the peak flow. At the peak, flow was 3.53 times greater than that at 16:00 hours (flow factor). The concentration of each metal concentration at the peak was determined by multiplying its concentration at 16:00 by this flow factor. The flow comparison was repeated for each time step and the calculation repeated. After 16:00, the effect of flow was small but metal concentrations remained elevated. From 16:00 to the end of the plume we interpolated linearly between the measured samples. For metals mass the plume was summed through August 6, 06:00.

Dissolved Metals Plume Reconstruction. Dissolved metals concentrations were reconstructed using a mixing model approach. The GKM effluent concentrations and volume were mixed in proportion to the background concentrations and flow volume in Cement Creek (Fig 3- 14). Backgrounds metals concentrations were based on several measurements in Cement Creek post event. Flow apportioned between the GKM effluent and natural streamflow during the plume and estimated pH are shown in Fig. 3-14. Initially, the plume made up almost 80% of the flow at Cement Creek. Estimated pH ranged from 3.5 to 4.8, varying as the slug moved through the creek.

Figure 3-14

Background metals concentrations were determined from water samples collected in Cement Creek upstream of the Gold King and downstream to the confluence by CDPHE on August 18, 2015. Background pH was estimated at 4.8 based on a series of measurements through Cement Creek. No pH was measured in Cement Creek during the Gold King release. The effluent pH was 2.93 during the August 15 sampling described earlier. Background flow was the baseflow prior to the arrival of the plume (12:30).

The low pH typical of Cement Creek was enhanced as the highly acidic "front" passed early in the plume, combined with the likely suspension of soluble mineral salts in the suspended load of the spill, probably resulted in the dissolution of metals as the plume passed through Cement Creek. Looking at the quality of mining-degraded watersheds, Nordstrom (2011) noted that initial flushes of water leaving watersheds after precipitation events were highly enhanced in mining-related solutes. This may be evident in the sample collected from Cement Creek at 16:00. After partitioning the flow and separating background metals from those in the effluent, it was notable that the dissolved concentrations of copper, zinc, aluminum and manganese increased substantially from sources other than the effluent. (Fig 3-15). This particular group of metals have active sorption isotherm edges in the pH range of 4 to 5 (Smith, Nordstrom 2011). Concentrations of arsenic and lead (pH in Cement too high to desorb) and nickel and cadmium (pH in Cement too low and metal already desorbed) were consistent with the effluent and appeared to have no additional sources.

Figure 3-15

With these conditions, concentrations of Al, Ca and perhaps Fe in Cement Creek, likely were buffered at nearly equilibrium with mineral phases including alunite, gypsum and perhaps jarosite, or similar minerals. Other than dissolution/precipitation of these soluble mineral phases, however, few other chemical changes likely occurred in the spill waters during the short residence time in Cement Creek, mainly ranging from 2 to 8.5 hrs.

Time-dependent dissolved concentrations in Cement Creek (C_{obs}) during plume passage were estimated using a general mixing model (Eq. 1) that assumes a time-invariant concentration in the mine discharge (C_{GKM}), time-invariant background concentration in Cement Creek (C_{bkg}) and the time-dependent flow ratios shown in Fig. 3-14. However, C_{GKM} first had to be estimated using observed concentrations at 16:00 in Cement Creek and re-arranging Eq. 1 into Eq. 2:

$$C_{\mathrm{obs}}(t) = C_{\mathrm{GKM}}\left(\frac{Q_{\mathrm{GKM}}(t)}{Q_{\mathrm{GKM}}(t)+Q_{\mathrm{bkg}}(t)}\right) + C_{\mathrm{bkg}}\left(\frac{Q_{\mathrm{bkg}}(t)}{Q_{\mathrm{GKM}}(t)+Q_{\mathrm{bkg}}(t)}\right) \tag{1}$$

$$C_{\mathrm{GKM}} = \left[C_{\mathrm{obs}}(16:00) - C_{\mathrm{bkg}}\left(\frac{Q_{\mathrm{bkg}}(16:00)}{Q_{\mathrm{GKM}}(16:00)+Q_{\mathrm{bkg}}(16:00)}\right)\right] \Bigg/ \left(\frac{Q_{\mathrm{GKM}}(16:00)}{Q_{\mathrm{GKM}}(16:00)+Q_{\mathrm{bkg}}(16:00)}\right) \tag{2}$$

To account for the "first flush" effect (Nordstrom 201), the concentrations of metals in the first two 15-min time steps were doubled after solving the mixing computations.

The simulated total and dissolved plumes for summed metals minus cations are shown in Figure 3-16 A and B. Both total and dissolved calculations are strongly dependent on streamflow and trace the flow. Similar concentration traces during the release were prepared for each metal.

Figure 3-16

The erosion of waste material outside the mine significantly increased the metal mass relative to what came from inside the mine. Onsite contractors determined that 10,000 cubic yards (7,600 m^3) were eroded from the hillslope and stream. Most was deposited in the North Fork and mainstem Cement Creek and was later recovered and stabilized.

The impact of the erosion on peak concentrations is illustrated in Fig. 3-17. Both dissolved and colloidal concentrations were significantly higher than the Gold King effluent when observed at 16:00 and were roughly 4 times greater at the peak with the techniques and assumptions that were applied. We note that there is considerable uncertainty with both colloidal and dissolved peak estimates with the general lack of data to confirm assumptions or the empirically modeled results. Higher values were selected when there was uncertainty.

The estimates of peak dissolved concentrations in Cement Creek were evaluated using Geochemists' Workbench® (see Appendix D for additional discussion of geochemistry of this analysis). The mixture produced at the estimated concentrations would be supersaturated with gypsum ($CaSO^4 \bullet 2H_20$) as well as other minerals. This result suggests that concentrations are most likely overestimated for at least some solutes. (See Appendix C).

Figure 3-17

Gold King Metal Mass Delivered to Animas River. Metals mass was calculated by multiplying flow by the concentration and summing for the period from August 5 12:45 to August 6 6:00. The period of flow was extended past the end of the flow defined period because concentrations of metals remained elevated until the next day even though flow levels did not.

The total estimated mass input of metals minus cations to the Animas River from Cement Creek was 490,000 kg of metals. Of this 475,000 kg was colloidal/particulate material and 15,000 kg was dissolved metals (Fig 3-18). The plume carried 47,000 kg of major cations (Ca, K, Mg, Na), and 11,600 kg of the major metals (Pb, Cu, Zn, Cd) and arsenic. The trace metals increased from 5 kg in the effluent to 875 kg in Cement Creek. The mass of dissolved and colloidal fractions of individual metals are shown in Fig. 3-19. The mass of individual metals is also provided in tabular form in Appendix G.

Figure 3-18 Metals mass.

We have no real way to validate this total, we can estimate the material eroded from the void scoured from the mine pile where most of the additional sediments would have come from. EPA contractors estimated the void volume to be 10,000 yd^3 (7,455 m^3). If bulk density ranged between 1.8 and 2.1 to, this would have created somewhere between 13,000 and 16,000 metric tons of material—mostly mine ores. Much of this material has been stabilized and removed from the North Fork Cement where much of it deposited near the mine site, but undoubtedly a portion of that material remains behind in Cement Creek. The estimated load seen at Cement Creek is reasonable given the erosion into the stream.

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CHAPTER 4: CHARACTERISTICS OF THE GOLD KING PLUME AS IT TRAVELED

The Gold King release generated a volume of acidic water and dissolved metals that travelled with and mixed into the ambient flow of the Animas River near Silverton CO. The plume that arrived from Cement Creek (RK 12.6) contained about 490,000 kg of dissolved and colloidal/particulate metals in a highly concentrated slurry carried in a slug of acidic water with pH of close to 3 initially. From there the Gold King plume traveled downstream over an 8-day period where it eventually reached Lake Powell. As it travelled, a number of physical and chemical processes would transform the composition and amount of material released from inside and outside the mine that remained in suspension or was left behind in the streambed as described in Chapter 3. The geochemical reactions generated the intense yellow color that drew international attention, and at the same time mitigated the acidity and chemical and physical makeup of the water as it flowed. As the Gold King plume traveled, the processes that determined its effects on water quality were dynamic and the spatial scale was challenging.

Figure 4-1 Photos of plume.

The plume would have changed speeds as it moved reacting to the slopes and characteristics of the river channel and would fill with new clean water from tributaries that would dilute the metals. The chemistry within the acidic slug would respond quickly as it mingled with the higher pH in the Animas River. Metals that were mostly dissolved in the mine would precipitate and form solids that would create the brightly colored iron oxides that intensified as it traveled. Trace metals would be swept up into the solids, reducing their availability for damaging effects. Some would be left behind in the streambed. New equilibria would continually evolve among the mix of metals remaining in solution. All of this would occur rapidly as the river moved at a pace of almost 2 mph over a distance equivalent to the trip between Boston and Washington or San Francisco and Los Angeles. Field crews would try to track it down as it moved day and night. No two places along the river would experience exactly the same plume.

Analysis of water quality characteristics and chemical transformations that occurred during migration of the Gold King plume requires considerations of the hydrodynamic and geochemical processes that transformed it as it moved (Fig 4-2). For those analyses to be credible, it is critical to accurately reproduce the time of travel and metal concentrations of the plume at each location along the river, especially at the peak. Concentrations fluctuated widely in a short time as the plume passed.

In this chapter the movement and metal concentrations of the Gold King plume as it passed through the Animas and San Juan Rivers was replicated using two methods. We used the software program (WASP) to develop a process-based model (WASP Model) that applied hydrodynamics principles to dynamically simulate the movement of the plume through the system. We also built a stationary model of the plume as it passed selected locations making full use of the water samples collected by the data providers introduced in Chapter 2. The dynamic and stationary models worked synergistically and in parallel to illuminate the key characteristics of metals as the plume moved through the system. Plume concentrations created by these models will be used in subsequent chapters to assess the metals transported in the water and deposited in the rivers.

Key characteristics to accurately reproduce during plume passage include 1) time of travel as it gives context to all of the samples that were collected at each location, 2) peak concentrations as they carry the bulk of the metals mass, and 3) the general shape of the plume as it determined the potential exposure to metals concentrations and estimates of mass transported and deposited (Fig 4-2).

Figure 4-2. Conceptual drawing of what this plume was

Observations of the Gold King Plume

We first develop a picture of Gold King plume behavior from a variety of observations and measurements during plume movement. The Gold King release into the Animas occurred during August as streamflow was receding from a summer storm several days earlier. Animas River flow originates high in the San Juan Mountains and was low to moderate during the Gold King release. The water was clear and constituents in the water were mostly the dissolved cations (Ca, K, Mg, Na). The slurry of metals and acid water that entered the Animas from Cement Creek near Silverton dramatically altered the content and coloring of the river that intensified as it traveled. The plume was readily observed through the entire 190 km length of the Animas over 2.5 days before it joined the San Juan River in Farmington NM. Visibility was lost in the extremely turbid waters of the San Juan that obscured observation and measurement. Most of what we learn about plume movement is understood from observations in the Animas River.

Plume movement through the upper Animas River was documented at the USGS stations. The Gold King release entered the Animas River at Silverton as both a plume of metal mass and a wave of water. The initial pulse of water at Cement Creek (Chapter 3) surged into the Animas River (Fig. 4-3A). On a normal summer day, Cement Creek contributes about 20% of the combined flow of the Upper Animas River and Cement at their confluence. That percentage rose to 50% in the first 15-minutes of plume flow. Within the Silverton area, the plume was rapidly diluted as all three major tributaries join before the USGS gage located about 2.5 down river from Silverton (16.4 RK from GKM source). A small wave of water associated with the plume diminished as it traveled but was measured as far as Durango at RK 94 before its signal was lost.

Figure. 4-3 Hydrographs

Integrating under the flow traces at each of these gages after removing baseflow reveals that the volume within the wave remained remarkably consistent at 1.2 million gallons (Figure 4-3B). This flow volume passed through Cement Creek in the first 45 minutes of the gage record discussed in Fig. 3-4). The gage records help to establish the travel time of the Gold King plume through the upper Animas River, but they do not directly assist with metals concentrations in the plume.

Field crews from the Mountain Studies Institute at the request of EPA intensively sampled the plume as it passed by Rotary Park in Durango at river kilometer (RK) 94.2. (Mountain Studies Institute 2016). (Data from this site is included in the EPAR8 source and this report.) These data provide an important anchor point for timing and metals concentrations at this mid-way point in the Animas River (Fig. 4-4). Anticipating the arrival of the plume in the late hours of August 6, crews remained stationary at one location collecting 6 samples from about 20:00 hours until 00:30 when it was thought that the plume had peaked. Crews did not measure the falling limb until 9 hours later. Besides setting the time, these water samples are especially helpful in showing the general pattern of metals concentration on the rising limb of the plume and the magnitude of concentrations at or near peak.

Figure 4-4

Plume travel through the lower Animas River was documented by five continuously recording sondes in this reach. Three were operated by the Southern Ute Indian Tribe (SUIT) on their reservation lands south of Durango to the Colorado border, while 2 were operated by New Mexico Environment Department (NMED) near Aztec and Farmington. The suite of sondes documented the passage of the plume through approximately 85 km distance with incidental measurements of specific conductance, pH and turbidity (Fig. 4-5). These instruments firmly established travel time through the lower Animas River. The sonde data did not directly relate to metals concentrations, which must be done with corresponding water samples collected at each location.

Figure 4-5 Sondes.

The traces from the 5 Animas sondes were normalized by their relative increase from a baseline established at the start of the Gold King plume so they could be plotted together in Figure 4-5A,B. The trace shows the relative rise and fall of specific conductance as the plume moved past each sonde. Normalization shows the plume had nearly identical shape as it passed each location, while the relative peak declined systematically with distance (Fig 4-5C).

These various data sources provided important perspective on the fundamental properties of the plume as it moved through the Animas, including travel time, peak concentrations and plume shape that define duration and the general distribution of concentrations and total mass. The observations shown in Figures 4-4 to 4-5 confirm that the plume moved as a coherent mass with metals concentrations that rose and fell with a beginning and tapering back towards pre-event concentrations over a period that may have lasted for several days.

Somewhat more of a surprise, there appears to have been an internal core within the longer duration plume where concentrations rose and fell quickly and that account for the highest concentrations of metals. This period is important for quantifying mass transport and exposure potential. This core appeared to have been concentrated within about 1.2 million gallons of the initial Gold King release that represented the first 1 hour of flow observed in Cement Creek. The shape of this core remained remarkably consistent as the plume traveled over the 200 km of the Animas River.

The various data and observations in the Animas helped quantify either travel time, peak concentrations or plume "shape" where they were available. However, none of these data were sufficient in and of themselves to establish all three at a location, nor could they be extrapolated to the rest of the river length without a means of adjusting for the physical makeup of the plume and the river along the way. Next we develop a set of models that enable us move the metals entrained in the Gold King plume incrementally through the rivers, while accounting for the transformations in chemistry, concentrations, and mass that occurred.

Modeling Methods to Simulate the Gold King Plume

We adopt two perspectives for modeling the Gold King plume. For a stationary perspective, we empirically reconstructed the plume at selected locations distributed along the river length from observed flow and water quality data and any other assisting information that was available. For a dynamic perspective, we applied a mechanistic fate and transport model (WASP Model) that moved the plume through the system at a fine scale of spatial resolution while it tracked transformations as they likely occurred. The two models work together to ensure that the dynamic representation is well grounded in field observations and that the empirical model fully understands timing.

Empirical Gold King Plume Model

The Gold King plume was empirically reconstructed at 12 sites distributed through the Animas and San Juan Rivers (Table 4-1; Figure 4-6)). Sites were selected near USGS gages and preferably at locations that were repeatedly measured by one or more organizations during the hours and days as the plume passed by. The Empirical Model made maximum use of the available observations from many data sources focusing on the water quality samples collected by the data providers. The model consists of the flow taken from the nearest USGS gage and the observed or estimated metals concentrations in each 15-minute period during the period of plume passage. All metals in the Total and Dissolved fractions were modeled with the approach described.

Table 4-1. Empirically modeled locations.

Figure 4-6 Location map

Plume reconstruction at each site required three steps to determine: 1) the arrival time of the plume; 2) the peak concentration of individual metals; and 3) interpolation between samples and the measured or estimated peak to complete the trace of the plume over the period of plume passage.

Ideally, each site would have a sample close to the peak and a well distributed set of samples that cover the rising limb of the plume (largely achieved in Durango, Figure 4-4). More commonly, samples were sparse (2 to 6 during the plume). Although many sites were sampled over several days during the plume, few samples managed to coincide with the passage of the inner core of the plume and almost none measured the peak. This was especially true at sites where the plume passed by during the night or in very remote locations. In places, multiple data providers collected at nearby but not identical locations. We merged data if sites were reasonably close to fill gaps where we could, adjusting for timing if necessary.

Peak concentrations were estimated with a basin-scale relationship between samples identified as close to the plume peak plotted as a function of distance from source. The relationships for arsenic and aluminum are shown as examples in Figure 4-8. All samples collected in the Animas River during plume passage are shown (not just at modeled sites.) Few were at or near the peak of the plume but 72 samples captured some part of the plume.

Those collected at or near peak were independently estimated from timing analysis (highlighted in red). Critical to this analysis were samples collected on the Southern Ute Indian Tribe reservation (SUIT) there were confidently labeled as peak by sonde observations.

The regressions show a dramatic decline in concentrations starting from the simulated plume in Cement Creek in the upper Animas and systematic decline through the entire Animas. This decline is due primarily to dilution and other physical and chemical processes that will be fully discussed in Chapter 5. The rapid decrease in concentrations with distance and at a location evident in Fig. 4-7 exemplifies the dynamic change that occurred as the Gold King plume travelled and the challenge of sampling it.

Regressions like those shown in Fig. 4-7 were fit to each metal to estimate its peak concentration. The estimated peak concentrations were often significantly higher than the samples at the site. We note, for example, that our estimate of the peak concentration at Durango was 25% higher than the highest sample collected there because the regression suggested it was higher and sonde information suggested the peak may have occurred 45 minutes later.

Figure 4-7

The process of determining the time of the peak was iterative using all available information, including sondes, flow, or by consulting WASP (described next). The Empirical Model used observed rather than modeled data when it was available. Each site was approached independently to assess the best approach.

Finally, the trace of metals concentration was completed by fitting lines between samples including the estimated or observed peak by one of several methods. The interpolation could be linear as illustrated in Figure 4-8, or it could be shaped by the flow trace, or by the normalized sonde shape factor shown in Fig. 4-5. A similar process based strictly on flow was used to determine the Gold King loading in Cement Creek described in Chapter 3. However, the usefulness of flow for this purpose rapidly diminished with the reduction in the hydrologic signature as the plume moved downstream. Note that the shaping factor does not determine the modeled concentrations except to guide the shape when there are few observations. The Empirical Model applied this process to model all metals in total and dissolved form.

There are uncertainties in all of these estimates. Errors could occur in establishing the timing, estimating the peak correctly and, when there are few data points in the record, interpolating between the measured values. The interpolation process was guided by "shaping" where possible, but there was not always a "natural" fit. Generally, the modeling philosophy was to error on establishing peaks that were too high rather than too low.

A strength of the Empirical Model is that it always fits through the observed data and it maximizes the use of field collected samples. In this regard, the Empirical Model provides the most reliable representation and much needed perspective to the water quality samples that were collected at or near each location. Without some way of knowing the timing of the plume, the relevance of the sample cannot be fully understood. The empirical model provides a representation of the Gold King plume at widely spaced locations.

WASP (Water Analysis Simulation Program)

To increase the spatial and temporal resolution of the plume as it traveled, we applied a process-based, mechanistic model that transported the plume through the Animas and San Juan Rivers. WASP is a modeling framework that allows the user to construct a surface water quality model for a system of interest in 1, 2, and 3 dimensions. WASP is used to develop a dynamic and spatially resolved mechanistic fate and transport model for environmental contaminants in surface waters and sediments. WASP allows for the time varying processes of advection, dispersion, point and diffuse mass loading, boundary conditions, boundary exchange, and equilibrium and kinetic processes.

WASP (v. 7.52) was parameterized to simulate the transport of water and metals from segment to segment through the Animas and San Juan Rivers while reacting to changing flow and hydrodynamic conditions and adjusting the chemical and physical properties of the plume as it moved (Fig 4-9). Developing the model for this application required a balance between complexity to capture the appropriate governing processes and simplicity to minimize necessary parameters to describe the increased number of processes and increased time and effort to implement the model. Increased complexity results in increased uncertainty. The specific model parameterized to simulate the Gold King plume in the Animas and San Juan Rivers created with WASP 7.52 is hereafter referred to as the "WASP" model for simplicity. Critical elements of model setup is briefly described here. See Appendix B for complete detail on model set-up and calibration.

Figure 4-9

Model Domain and Setup. The WASP model domain was bounded by 3 USGS gages: the Animas River upstream of Cement Creek (USGS 09358000), the San Juan upstream of the Animas River (USGS 09355500), and Cement Creek just upstream of the convergence with the Animas River (USGS 09358550). The flow at the Cement Creek gage and the metals load and concentrations from Gold King that were developed in Chapter 3 served as the boundary condition for the start of the Gold King plume transport.

The model domain consists of two sets of WASP segments, one that represents surface water and one that represents sediments. WASP spatially divided the river course into 229 segments delineated based on the NHD Plus dataset. The model decides the length of each segment, varying them to maintain approximately equal travel times to reduce numerical dispersion and minimize numerical instabilities in the computations. Segments averaged 2.45 km in length but varied from 0.9 to 4.7 km. The variation indicates the spatial variability in flow velocity induced by varying river conditions. Each spatially defined segment has two individual layers—the water column and the sediment. Materials transported within the water column are sequentially passed to the next downstream segment. Materials are also transferred between the water and streambed segments.

Figure 4-10

WASP Model Parameterization. The general type of parameters required to set up the WASP model are listed in Table 4-2. A primary parameter is the flow in river. Flow was obtained from the 12 USGS gages located within Animas and San Juan modeled segments (Table 4-2; Fig 2-7.). USGS gages are spaced closely within the Animas River (27 km) and the San Juan River (60 km) enabling robust flow transport with minimal uncertainties in this important characteristic for the Gold King application. Rather than adjusting flow at incoming tributaries, we compared flow between the nearest downstream gage and increased or decreased the flow in 3 spatial increments through the reach. This may have resulted in local segment level errors in flow or deposition but any errors were corrected at each gage.

Table 4-2.

WASP simulates streamflow using the principles and standard equations for conservation of mass and momentum. The channel characteristics important in this process include width, depth and slope were parameterized using data from NHDPlus. Hydrology flow coefficients were determined using the hydraulic geometry data published with each USGS stream gage. Hydraulic geometry relationships that relate the depth and width to flow were determined using power equations based on regressions of available gage cross-section data (Leopold and Maddock, 1953 as cited by Chapra, 1997).

The only part of the flow modeling that was calibrated was for stream velocity, by adjusting Manning's roughness coefficients and the velocity exponent. Manning's roughness adjusts velocities to account for various forms of roughness that slow river flow. For a given slope, Mannings roughness coefficient (n) was adjusted until simulated and observed velocity matched. The calibrated n varied within the typical ranges reported for rivers (0.12 to 0.35). The velocity exponent affects how velocity changes as a function of flow. We adjusted the velocity exponent within the bounds of the coefficient estimated through the regression of observed data.

Metals Composition. It was important to meet project objectives for the model to account for the geochemical transformations that occurred during plume movement at some level of resolution. Metals change from dissolved to particulate form occur through complex geochemical reactions including sorption, oxidation, and precipitation. Some fate and transport models can account for these processes, but the data needed to perform sophisticated equilibrium and speciation transformations were non-existent during Gold King plume movement. Therefore, rather than explicitly modeling these processes, we adopted a more general approach using the WASP TOXI module to account for the partitioning of metals between dissolved and colloidal/particulate phases using a lumped parameter treatment of the partitioning coefficient (Kd). K_d was determined using total particulate metal concentrations and the unfiltered and dissolved concentrations of the individual metal of interest usingthe empirical model's estimate at the plume peak (See Appendix B.) We then used a regression to estimate Kd as a function of river distance, as Kd changed as the chemistry of the plume changed traveling downstream. There was a specific Kd as a function of distance for each of the four metals simulated (As, Cu, Pb, Zn). The WASP TOXI module also addressed diffusion between the water column and the sediment pore water.

Deposition and Entrainment. The ability to deposit and entrain the materials carried in the Gold King plume was also very important to meet project objectives. WASP uses a constant settling velocity based on Stokes' law to partition materials to the bed or entrain them during higher flows. To determine the settling particle size, we again used the results from the Empirical Model to determine the effective particle size that determines the selection of settling velocity.

The mass of metals carried past each empirically modeled location during the plume (Table 4-1) was determined by integrating concentration and flow under the concentration traces. We then back-calculated from these mass estimates to identify what particle sizes matched to the settling velocities would produce the loss of mass between stations. The estimated particles were within the silt-size fraction, which was a very reasonable size range for what would be expected from the precipitates that generated the bright yellow color. This result not only helped calibrate the WASP model but provided some corroboration to the Empirical Model as well.

WASP was applied to simulate the dissolved and total fractions of the metals summed and the individual metals Arsenic, Lead, Copper, and Zinc.

Summary of the Modeling Approaches. The two modeling approaches simulate the metals composition of the Gold King plume including the dissolved and total fractions of metals. There are a number of synergies and differences between the two approaches (Table 4-3). The Empirical Model simulated all the metals while the WASP model simulated a subset. The Empirical Model produced the plume at just 12 locations. The WASP model could locate the plume within the river system within its 2-km reaches or its status at any location at any time. After calibration, the WASP model provided better precision on travel time than any other technique. The Empirical Model was built entirely with observed water sampling while WASP estimated and adjusted concentrations reflecting physical and geochemical processes encountered in the river as the plume moved.

Table 4-3 Model synergy

There are a number of synergies between the models. WASP used key Empirical Model results to calibrate critical processes, thus linking WASP calibration firmly to observed data. These included partitioning of metals to dissolved and solid phases and particle settling velocities. WASP informed the Empirical Model about plume arrival times, especially in the San Juan River where there were no clear observations of the plume. The Empirical Model takes no other information from WASP simulations. Similarly, WASP was not calibrated (or validated) against sample concentrations directly. The two models do not produce the same concentrations or estimates of mass where they meet and we made no attempt to make them do so.

There are many uncertainties in estimating plume composition and travel. The two modeling approaches provide a range of estimates that reflect the strengths of using observed data and the strengths of using process-based tools when data is limiting. The two models together are the basis for quantitative analysis of the transport and fate of Gold King metals in the Animas and San Juan Rivers in the following chapters.

Plume Movement Through in the Animas and San Juan Rivers

In this section we discuss the movement of the Gold King plume through the Animas and San Juan Rivers, based on the modeling and observations that went into building them. We compare modeled simulations at individual locations and discuss the general movement of the plume through the river as a whole enabled by the modeling.

Animas River Gold King Plume Movement. Characterization of the Gold King plume as it traveled through the Animas River was strong due a variety of corroborating information, not the least of which was its visibility within the Animas. There was no confounding background turbidity, water quality samples were collected at a number of locations, and sondes firmly anchored the travel through the lower Animas.

The travel of the Gold King plume through the Animas River was a major media event that riveted public attention. Early reports of the plume's progress was illustrated in the Denver Post marking sightings by location along the upper Animas (Fig. 4-12). We have plotted the GK WASP simulated plume at 5 locations at the observation time reported in the newspaper account. In each case, GK WASP placed the observer in the leading edge of the plume, typically after water concentrations had already started to increase. This may simply reflect the arrival time of the observer, but may also indicate that concentrations needed to achieve some level before the plume was clearly visible to an observer.

Figure 4-11. Photo

Figure 4.12 Observations

The plume simulated at six Animas River locations by GK WASP and the Empirical Model are shown in Fig. 4-12. The colloidal fraction of all metals summed is shown, along with whatever shaping factor was used by the Empirical model. Note that the shaping factor does not determine the modeled concentrations on the secondary axis except to guide the shape when there are few observations. With the exception of Durango, there were few observations during passage of the plume core.

Passage of the plume past the Animas sites reconstructed by the Empirical Model and WASP are shown in Fig. 4-13. At some locations both models produced the same peak, while at others they did not. The WASP Model tends to produce a longer duration plume that appears to be roughly bell-shaped, with a steeper rise and a slower decline, with higher concentrations for longer periods on the rising and falling limbs. This is probably caused by numerical dispersion, which can cause widening of plumes on the leading side of the plume and lower simulated peak concentrations. The Empirical Model created a narrower rise and fall of concentrations than WASP. This reflects the use of observed data including water samples, sondes or flow to shape the plume. However, this same shape also fits the observed rising limb at Durango well, suggesting this is a better representation of actual concentrations. The two approaches offer a range of concentrations reflecting uncertainties in both modeling and data availability. We believe that the Empirical Model reflects the passage of the core of the plume and bulk of metals better because it is tied to field observations, but that WASP may reflect the experience of observers who saw tinted water with low concentrations of metals for longer periods than the Empirical Model would suggest.

Figure 4-13

San Juan River Gold King Plume Movement. Quantifying travel time and concentrations of the Gold King plume once it entered the San Juan River was very problematic. Water released from the Navajo Dam created streamflow conditions consistent with a moderate storm which also generated high sediment loads that visually obscured the Gold King plume and significantly raised the "background" level of metals. We will show in Chapter 6 that the sediment loads brought comparable levels of metals from the San Juan River at Farmington as the Animas brought to it carrying the GKM plume. The plume was visibly obscured by the high sediment loads, and the metals signature in the samples from the Gold King release was also blurred by the "background" sediments in the river. This was especially problematic since plume concentrations were also much lower than experienced in most of the Animas. Reconstructing plume movement through the San Juan required modeling.

Figure. 4-14 Photos

There was one sonde monitoring the San Juan River in Farmington. Turbidity from the instrument shown in Fig. 4-15 oscillated widely during the time leading up to, during and after the passage of the Gold King plume. The simulated timing of the plume is superimposed on the turbidity trace by centering the Sonde Shape Factor (e.g. Fig. 4-5) at the peak arrival time suggested by GK WASP (Aug 8 13:00). An increase of turbidity of about 200 ntu occurred at this time and the duration of this period of elevated turbidity was consistent with the sonde shape factor that represents the plume core. This suggests ethe estimated arrival time was correct. Also noteworthy was that turbidity induced by the Gold King plume was well within the normal turbidities observed in the river in this period of higher flow accompanying the dam release.

Figure 4-15

The visibility of the plume was lost relatively quickly as it traveled down the San Juan and the waters of the Animas thoroughly mixed with the San Juan, further diluting the plume. Unlike the Animas where there was no background metals load and unusually high concentrations from Gold King, the San Juan River had high background metals concentrations and low concentrations from Gold King. In the San Juan, we're tracking both the background sediment and any influence from the plume that may be buried within it. GK WASP really assists understanding the GKM plume in the San Juan and it was the only method that could determine the plume arrival over the next 400 kilometers of travel.

WASP was set up to run in two modes in the San Juan. One brought the Gold King plume into the San Juan River assuming no background sediment and associated metals mass, or as if the Gold King plume was moving through distilled water (GKM pure). This allowed us to look at what the metals concentrations from the Gold King plume alone. In the second mode, the Gold King plume was mixed with the incoming metals load from the Upper San Juan (GKM mixed). In this mode WASP modeled what was actually in the river when the plume moved through including the background metals.

To simulate the plume at San Juan locations, the Empirical Model centered at the suggested peak from GK WASP. The Empirical Model had no way to estimate the peak from samples as it did in the Animas, so it simply fits a line between observed sampled within a 48 hour period around the peak. Simulated plumes at 5 San Juan locations are shown in Fig. 4-16.

Figure 4-16

WASP suggests that the plume continued to travel through the San Juan River as coherent unit although at very low concentrations, especially relative to the background concentrations in the river. At Farmington, the summed colloidal metals from Gold King at peak were estimated to be about 25 mg/L and by Mexican Hat they were 10 mg/L. Background colloidal metals were about 200 mg/L.

We ended simulations at Mexican Hat due to lack of data past this point due to lack of data and low concentrations.

We set initial concentrations to 0 throughout the system so that concentrations rose and fell solely due to the passage of the release plume. This eliminated background concentrations of dissolved calcium, potassium, magnesium and sodium that are the primary constituents in the water at this time of year. The upstream boundary condition for total particulate metals in the San Juan River is upstream of the confluence with the Animas River and is based on observations in the lower Animas in the San Juan immediately downstream from the confluence.

General Overview of Gold King Plume Travel

The challenge for modeling was to simulate the peak concentrations, travel time, general shape characteristics of the Gold King plume, and the travel time through the system. Modeling enabled integrated quantification of plume characteristics and revealed general patterns of travel within the Animas and San Juan Rivers that was not possible from the field sampled data alone.

Peak concentrations of metals were very high when the Gold King plume entered the Animas River at Cement Creek. Peak concentrations dropped by 4 orders of magnitude by the time the Animas River joined the San Juan and continued to decline as it passed through this river (Fig.4-17). Both models agreed on the magnitude and distances over which this decline occurred. Chapter 5 will further explore longitudinal trends in water quality and mechanisms that contributed to the changing metals composition.

Figure 4-17.

WASP simulations suggested that plume shape changed during travel. Peak concentrations decreased while the duration of elevated concentrations increased (Figure 4-18). The effective length of the plume in Silverton was on the order of 10 hours, while it may have required 50 to 80 hours for the now much lower concentration plume to pass through the San Juan. The Empirical Model generally models for a shorter period than WASP. Evidence from continuously measuring sondes suggests that bulk of the plume passed more quickly (within 12 to 18 hours) at every location.

Figure 4-18. Duration and shape figure.

The plume traveled through the Animas and San Juan Rivers over a period of 8 days at an average velocity of about 3.1 kilometers/hr or 2 mph. WASP appears to produce a reliable record of the travel time and can provide the timing at every place along the river. Both models agree on the time that the Gold King plume peaks arrived at their common locations (Figure 4-19.). The sonde data in the lower Animas River firmly anchored the time of travel through this point in the travel. There was less evidence to corroborate travel time through the San Juan, but samples collected near the estimated arrival times appeared to show small increases in metals concentrations as predicted by WASP.

Statistics of the arrival of the peak at a number of sampling locations for data providers are provided in Table 4-4. Travel times reflect the flow conditions during August 5 to 13. We note that initial estimates based solely on the flow at the USGS gages proved to be too fast. This schedule would likely reasonably estimate the travel time of a similar release that occurred at similar level of flow, or GK WASP can simulate at other flow levels and adjust travel times accordingly.

Figure 4-19. Travel time in graphics form.

Table 4-4. Plume schedule.

CHAPTER 5. WATER QUALITY OF THE GOLD KING PLUME AS IT TRAVELED

The combination of observations organized by empirical and analytical modeling enable characterization of water quality as the Gold King plume moved through the Animas and San Juan Rivers. Chapter 4 showed the dynamic movement of the plume movement and its general metals content at a location as it passed.

In this chapter we examine metals concentrations and processes that affected them as the plume travelled in greater detail. Once the slug of acidic metals laden water moved into the Animas River from Cement Creek, the river water would naturally mitigate the acidity that would stimulate changes to metals composition, mass, and potential toxicity in the water. Two perspectives of the Gold King release are addressed. Concentrations of metals in the release are important for understanding potential exposure impacts. Translating concentrations to mass transported during the plume is important for tracking the fate of the Gold King metals (Table 5-1.) In this chapter, observed and modeled data to characterize metals concentrations emphasizing individual metals, and evaluate the transformations that occurred as the plume flowed. Chapter 6 addresses the fate of the Gold King plume mass.

Table 5-1. Plume analysis organization.

Longitudinal Trends in Water Quality

Modeled Peak Concentrations. The peak concentration of metals simulated with water quality modeling decreased by orders of magnitude as the plume flowed through the Animas River between Cement Creek and Farmington (Fig. 5-1). Most of the decline occurred within the first 100 km of travel and concentrations were generally much closer, though still elevated, as the plume passed from the Animas to the San Juan River. Concentrations of metals generally increased during the time the plume travelled through the San Juan River. Sampled data collected in the time from of the plume (Aug 5 to 10) were within the simulated peaks. The wide spread at individual locations highlights the wide fluctuation in the relatively short time of plume passage shown in Chapter 4.

All of the metals in both total and dissolved fractions showed the general pattern illustrated for the summed total metals shown in Fig. 5-1. Modeled peak concentrations of the dissolved and total fractions of arsenic, copper, lead and zinc are provided in Fig. 5-2. We will show results for these 4 metals throughout the report.

Figure 5-1.

Figure 5-2.

It is important to note that from a water quality perspective, the Gold King plume was experienced differently in the Animas and San Juan Rivers. As the plume moved through the Animas River, flow was low and typical of August. There was a very influx of metals concentrations from the plume that entered from Cement Creek into a background metals load made up primarily of dissolved cations including calcium, potassium, magnesium and sodium. Conversely, the flow in San Juan was equivalent to a moderate storm event with the release from the Navajo Dam. This generated high background sediment with commensurate metals load and turbidity. At the same time, metals in the Gold King plume declined through the Animas due to a number of factors. These differences in hydrologic conditions affected longitudinal patterns of metals in the rivers. We will separately look at patterns of metals concentrations in the Animas River and San Juan Rivers.

ANIMAS River Water Quality During the Gold King Plume

Within the Animas River, metal concentration in general declined by three to five orders of magnitude from the concentrations that were introduced from Cement Creek at the peak of the plume (Chapter 3).

The strong decline in metals concentrations in the Animas River reflected natural processes that mitigated the acidity and metals concentrations observed in the water. Three important factors contributed to the large decline in metals concentrations in the Animas River:

- Dilution reduced concentrations of all metals in both the total and dissolved fractions. Dilution did not affect the mass of metal released from Gold King but lessened the potential exposure to very high concentrations;
- Geochemical reactions transformed the dissolved metals entrained in Cement Creek to colloidal/particulate solid forms, making them part of the large colloidal/particulate load entrained in Cement Creek. The geochemical reactions affected how much of the metals were dissolved and solids, but did not affect the mass that had been released from Gold King.
- Deposition of the solids formed from the chemical reactions reduced the concentrations of colloidal metals (total) carried in the water column and transferred them to the streambed. Deposition changed the concentration and mass of solids transported down the river. These settled materials could potentially be released during later flows.

Total and dissolved concentrations of 4 metals in water samples are shown in Fig. 5-3 and Fig. 5-4, respectively. The line shown on this plot is what concentrations from dilution from incoming flow would produce.

Figure 5-3 Longitudinal plot of total metals

Figure 5-4 Longitudinal plot of dissolved metals.

Dilution. Metals concentrations in the Gold King plume were strongly diluted with incoming flow to the Animas River as the plume flowed south. WASP was effective in quantifying dilution because it tracks hydrologic change along the river. Dilution was already a significant factor within a short distance from Cement Creek after the convergence of the three major tributaries that comprise the upper Animas watershed in the vicinity of Silverton (Fig. 5-5), Flow was 88% more dilute from the Upper Animas River and Mineral Creek within the first 4 km of travel. But the time the plume reached Durango the volume of water that originally received the release was less than 1% of the river flow. Flow doubled when the Animas joined the San Juan at Farmington, further diluting the Gold King plume.

Figure 5-5

The concentrations of all metals in dissolved and colloidal/particulate fractions were equally reduced by dilution. All the observed concentrations, including the few at the peak of the plume were within the range that could be expected from dilution alone. Over the course of the Animas River, dilution generally accounted for at least 2 orders of magnitude reduction in total and dissolved metals concentrations.

Geochemical Reactions and Transformations. The release from the Gold King mine spilled large volumes of a solution with high concentrations of dissolved metals and low pH from Cement Creek into the upper Animas River at Silverton. The Animas River is buffered by calcareous bedrock upstream from Silverton (Desborough and Yager 2000, Schemel and Cox 2005) and as it travels southward through numerous pre-Tertiary sedimentary beds of limestone and calcareous shale (Yager and Bove 2002). The alkalinity of these waters was important for the potential to neutralize the acidity of the Gold King release.

Figure 5-6. Photos

Neutralization of the mine release acidity initiated a series of geochemical reactions that would systematically alter the makeup of the Gold King plume as it mixed with the river's alkaline and oxygenated water. The same principles are applied in treating AMD as naturally occurred as the plume travelled through the Animas River. The major metals entering from Cement Creek in dissolved form, including iron (Fe^{3+}), aluminum ($Al^{3+)}$ and manganese (Mn^{4+}) would undergo a series of oxidizing reactions that would nucleate metal oxide minerals. These minerals, referred to generally as "yellowboy", gave the river its intense yellow color. As the reactions proceeded, the color would intensify as the reactions generated additional acidity.

The reactions would progress creating a series of minerals, some of which were short-lived and unstable under evolving conditions within the plume, and some of which were more stable and persisted. Among these would be the iron oxide (ferrihydrite) and calcium sulfate (gibbsite), which were likely the dominant minerals in the yellowboy. See Appendix C for more detailed discussion of the geochemical reactions within the plume.

A variety of factors determined the minerals that formed including the composition and volume of the metals in the plume as well as the availability of the neutralizing anions such as sulfate and calcite that nucleated with them. A primary controlling factor in these reactions was the availability of hydrogen ions (pH). Because of the large volume of AMD to consume, these reactions proceeded over many hours and changed along the river as reactions progressed, imparting a varying signature along its course.

As the pH increases, the reaction times of the processes speed up. Using the kinetic data supplied by Singer and Stumm (Singer and Stumm 1970), the ferrous oxidation half-life falls to 7 hours at pH 6, 4 minutes at pH 7 and 3 seconds at pH 8 (Table 5-3). The kinetics of the reactions in the river environment enhanced oxidation and would favor generation Fe^{3+} through oxidation of Fe^{2+} that would foster precipitation of amorphous ferric-oxide mineral phases. As the metal oxides precipitated they would scavenge the other metals present in lower concentrations. The rate at which individual metals were sorbed into the oxides would also depend on pH (Smith 1998). Each metal has a range of pH that favors dissolved metal ions coming out of solution and sorbing to solid surfaces (termed the sorption edge) (Fig. 5-7).

Table 5-2.

Figure 5-7.

The kinetics of the reaction in the river environment would favor creation of minerals in amorphous colloids. A colloid is a non-crystalline substance consisting of large molecules or ultramicroscopic particles of one substance (e.g. iron oxide) dispersed through a second substance (e.g. water). Colloid particles are small (10^{-6} to 10^{-3} cm) and carried in suspension, and cannot be separated out by ordinary filtering. Examples of liquid colloids include paint or milk (Fig. 5-8).

Figure 5-8. Photos of colloids, precipitates

The colloids formed in the Animas River would be electrostatically charged favoring suspension. They also could aggregate into larger particles that can settle to the streambed. Yellowboy staining is common in the streambed of the Animas River near Silverton from ongoing AMD (Schemel *et al.* 2000; Ranville and Schmiermund,1999; Schemel *et al.* 2007). The Gold King plume deposited various minerals, predominantly iron oxides, along the length of the Animas River, as will be discussed in Chapter 6.

Bare metal ions present in solution such as Cu, Zn, Pb, Cd, and Ni readily bind to charged surfaces to achieve more chemically stable crystalline and solid forms (Schemel *et al.* 2007). The metal ions present in AMD "sorb" to the iron oxide precipiates as well as sediments and organic matter through chemical and electrostatic bonding.

The amorphous colloidal particles can range in size from 0.001 to 10 microns with varying degrees of internal stability. They are readily suspended in streamflow but they can also be entrapped in the streambed when provided an opportunity to settle.

Sorption (binding dissolved to solid surfaces) is regulated by pH, and individual metals sorb at different levels of pH (Fig 9). Sorption of individual metals in an AMD solution can be affected by the mixture and concentration of metal species (Smith 1999). Metal sorption may be transitory if conditions change to favor desorption in which sorbed metals return to solution. Change in factors like pH, dissolved species and temperature may trigger desorption reactions (Smith 1999). Metal ions also sorb directly onto the surfaces of sediments by chemical bonding to reactive sites on particle surfaces. Minerals have varying capacity in the amount and strength of binding surfaces (Smith 1999). Some such as clay are better sorbents than others.

Acid Neutralization. The upper Animas River flows through calcareous rocks before joining Cement Creek. (See geologic map of the headwaters, Fig. 1-3). The Animas is well buffered with moderately alkaline pH and conditions vastly enhanced the oxidation reactions in the river and initiated the precipitation of the oxide minerals as soon as the plume entered. For the first 15-minutes flow from Cement Creek carrying the plume made up 50% of the combined flow of the Animas and Cement Creek. The pH of Cement Creek was probably close to that measured at the mine (~3) and the pH of the Animas River is generally varies but is approximately 6-5 to7.0 at this location.

We performed a series of geochemical computations to support this analysis of acid neutralization and to model of the precipitation reactions were modeled thermodynamically. See Appendix C for an in depth discussion of these processes. Here we will demonstrate large scale patterns in metals concentrations that could be observed in the water sampling suggesting by application of geochemical principles. The analysis focuses on characteristics at the empirical sites and analysis is based on observed and modeled data.

Background pH in the river also increases in the downstream direction as waters draining sedimentary rocks increasingly enter the river. The water pH fluctuates on a daily and annual basis; just prior to the plume pH was about 8.7 in the lower Animas River. Observations of pH were collected at several locations along the Animas River at or near the peak, including at the sondes located in the lower Animas. Fig. 5-9 shows a virtually linear increase in pH as the plume traveled for the first 100 km. River pH generally reached ambient pH at around 110 km, although small increases in pH were seen in the lower Animas River as the plume passed.

Figure 5-9. pH of the Animas River observed during passage of the plume.

Given this geologic setting, and using the available data, saturation indices (SIs) were calculated, using thermodynamic data reported in Parizek, and White *et al.* (1971) for calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) downstream of the Gold King Mine including Cement Creek, the Animas River and into the San Juan River A maximum estimated load of acidity in the mine release was ~54000 kg as $CaCO_3$ (See Appendix C for detailed explanation of these estimates).

The saturation status of calcite is shown in Figure 5-10. Computations of alkanity of the release waters suggests that the dissolved acidity of the release water would be roughly balanced by Animas flow over 2 days. The actual time to neutralization of the release waters in the Animas could have occurred more quickly if we have underestimated the amount of alkalinity added with downstream tributary inflow or overestimated the acidity load of the release.

Figure 5-10 Calcite, Dolomite

Negative SI values indicate that water was undersaturated with a mineral phase, values of near zero indicate the water roughly was in equilibrium with a mineral phase, and positive SI values suggest the mineral should precipitate from solution. Figure 5-11 indicates that the Animas was variably undersaturated with respect to calcite and dolomite (not shown) immediately downstream of Cement for about 100 km (suggesting the presence of acidity), but that Animas remained roughly saturated with these alkaline minerals for most samples >150 km (suggesting neutralization of acidity in these locations).

These computations confirmed by the pH observations show that essentially all of the release acidity was neutralized in the Animas River within about 100-150 km of stream distance from Gold King Mine. Active transitioning of dissolved to colloidal/particulate phases would occur concurrent with the neutralization. Water sampling confirmed that this transition occurred (Fig. 5-9). Approximately 15,000 kg of dissolved metals were delivered from Cement Creek to the Animas River (Fig.3-18). The mass of dissolved metals computed from the empirically reconstructed plumes along the Animas decreased and colloidal/particulates increased systematically within the first 100 km of travel through the Animas. Dissolved metals from the plume were completely sorbed into the iron and aluminum oxides by Aztec NM (RK 165km). The cumulative distribution follows the calcite saturation trend.

Figure 5-11

The dissolved trace metals in the release would be incorporated into the iron and aluminum oxides as impurities. The changing pH of the river determined the spatial patterns of dissolved versus colloidal/particulate composition for individual metals. We expected the transformation of the metals to occur over a distance reflecting where the pH passed through each metal's sorption edge range shown in Fig. 5-7. A longitudinal trend in the transition from the dissolved to colloidal form as pH increased was observed as shown in Fig. 5-12 (As>Pb>Cu>Zn>Ni>Cd). This pattern in dissolved to colloidal fraction was observed in the individual metals at the peak, as shown in Fig. 5-12. The individual trace metals lead and arsenic were in solid form quickly within the distance where pH exceeded 4. Dissolved copper was largely sorbed when pH reached 6 at Durango. Dissolved zinc and cadmium continued in dissolved form to RK 132 consistent with achievement of background pH close to 8 Nickel showed significant fractions as dissolved throughout the Animas, increasing somewhat in the lower Animas.

Figure 5-12

As the Gold King plume reached the confluence with the San Juan River at its peak, the yellow color was still highly visible. However, the dissolved metals had been sorbed into the colloidal precipitates and there was essentially no Gold King dissolved metals concentrations passed to the San Juan River. The dissolved concentrations of metals in the Animas River were very low generally (<5 ug/L) and at or near background levels (Fig 5-13.). Background was determined from later samples collected 3 weeks after the plume.

Figure 5-13.

The colloidal/particulate concentrations (represented by the total fraction), remained significantly elevated relative to background as the peak of the plume where the Animas joins the San Juan in Farmington (Fig. 5-14). Although at considerably lower concentration than observed in the upper Animas, the concentrations of all metals remained significantly higher than background for the Animas, especially iron and aluminum. As would be expected with the colloidal particulates formed during neutralization, the total aluminum and iron concentrations were very high. Total lead, copper, arsenic and zinc were well above background levels.

Figure 5-14.

In summary, by the time the Gold King plume flowed from the Animas River into the San Juan River, all of the dissolved portion of metals had transitioned to solid form and been incorporated into the colloidal/particulate yellowboy. Total concentrations of metals had also declined by 4 to 5 orders of magnitude. For example, the empirically estimated concentration of all metals summed (less major cations) ranged within the Animas River from 6,920 mg/L below Silverton to 50 mg/l in Farmington. Concentrations were reduced due to dilution from incoming fresh water, but also from settling of the colloids and aggregates to the riverbed. The mass and distribution of this material will be quantified in Chapter 6.

Water Quality in the San Juan

The high concentrations of metals released into the Animas River at Cement Creek significantly raised the concentrations of all metals. By the time the plume reached the lower Animas River, it was still highly visible but metals concentrations had declined by several orders of magnitude (Fig. 5-15). The visibility of the plume and relative effects on water quality changed significantly as the Gold King plume moved into the San Juan River. The San Juan River generally carries more sediment than the Animas River, as visible in the aerial image in Fig. 5-16. Anticipating the arrival of the Gold King plume, the Bureau of Reclamation has released water from the Navajo Dam. Both rivers had relatively high and almost identical flow as irrigation and other water withdrawals had been curtailed on the Animas. During high flows, the San Juan historically has a high sediment load. Suspended sediment measurements taken on August 9 as part of the river sampling showed a significant elevation of suspended sediment in the San Juan, that continued to increase as the river flowed westward. The plume was visible when it first entered the San Juan (Figure 5-15) but became difficult to visually detect as it travelled and mixed with the sediment.

Figure 5-15. Photos

Figure 5-16 Graph of sediment concentration increase

Total metals concentrations were elevated when then entered the San Juan from the Animas, but were largely equalized in the San Juan due to the background of metals in the sediment load. Summed total metals concentrations (minus cations) Is shown in Fig. 5-17 in the Animas and for 5 locations where the plume was empirically modeled in the Animas. Peak concentrations in the San Juan equaled that in the Animas and tended to increase somewhat as the San Juan flowed westward.

Figure 5-17

Patterns for individual metals varied. Iron was the major constituent of the metals load and remained constant through the San Juan. Aluminum increased significantly throughout the length of the San Juan. Total lead, zinc, copper and arsenic decreased, while chromium and cobalt increased somewhat (Fig. 5-18). Dissolved concentrations delivered to the San Juan during the Gold King plume were low and remained low as it passed through the San Juan River (Fig. 5-18).

Figure 5-18.

Metal Signature from Gold King

The ability to detect the Gold King plume in the San Juan River was hampered by the high sediment load and associated metals that arrived from upstream of the Animas confluence, combined with the relatively low concentration in the plume at this point. We looked for correlated parameters that could serve as a "marker" or signature of the Gold King plume that would isolate it from background levels in the San Juan.

The relationships between trace metal concentrations and those of aluminum and iron from the same water samples were useful for this purpose. The rationale was that aluminum and iron are relatively abundant elements in soil and sediments and should be indicators of sediment content when direct measures of sediment are not available. Iron and aluminum were also the major constituents in the Gold King release, but the plume was also significantly enriched with trace metals. Fig. 5-19 shows the relationship between iron and aluminum to suspended sediment concentration in sampling during the Gold King Plume. While there were relatively few samples where sediment and metals are reported either prior to, during, or after the Gold King event. However, there are many samples in all three time frames where aluminum and/or iron is reported with the trace metals.

Figure 5-19.

The correlation between aluminum and four trace metals are shown in Figure 5-20. All samples collected in the San Juan River during and after the plume show a strong relationship between the metals shown, with similar relationships for those not shown. Aluminum concentration in the San Juan River ranged over 6 orders of magnitude during the Gold King Plume and during several storms occurring in August and September 2015 following the event.

The trace metals show systematic increase in concentration with aluminum. Similar relationships occur with iron (not shown). These relationships indicate that the metals present in the soils and sediment are mobilized with sediment during higher flows, and are observed in a relatively constant proportion with the sediment. When sediment is present in high concentrations, trace metals will also be present in predictable proportions.

Figure 5-20. Total aluminum correlations to trace

The metals concentrations of samples thought to be collected during the plume based on the WASP and empirical modeling analyses are highlighted as the yellow triangles. The concentration of aluminum during passage of the plume ranged from 10,000 and 100,000 ug/L. Based on the non-plume data, lead for example normally would range from20 to 100 ug/L. The lead concentrations in a number of plume samples were significantly higher (up to 300 ug/L). Conversely, total copper and arsenic were within the normal range of variability during plume passage. This correlation method was the main way we were able to confirm the passage of the plume in the San Juan within the background level of metals associated with the sediments also carried by the river.

Dissolved metals were also well correlated with dissolved aluminum and iron (Fig. 5-21), although at much lower concentrations. There was no indication of elevated concentrations of dissolved lead during passage of the plume. This was also suggested by the comparison of lead concentrations at tge junction between the Animas and San Juan Rivers.

Figure 5-21. Dissolve aluminum correlations

Limiting the samples to individual location shows the same general relationship. Lead was evident in the plume as it flowed from Farmington to Four Corners at RK 297 (Fig. 5-22). The total lead signal diminished by Montezuma and was lost by Mexican Hat where there was good sampling coverage of the plume. Arsenic showed a similar pattern as lead, although arsenic could not be detected after Farmington (Fig. 5-23).

Figure 5-22 Lead

Figure 5-23 Arsenic

The same correlations between trace metals and aluminum were evident in the Animas River, the Gold King plume signature was much different due to the higher metals concentrations (Fig. 5-24). Concentrations of both aluminum and trace metals were very high during passage of the Gold King plume and greater than any observed in the historic data available within the river system.

Figure 5-24. Total metals in relationship to aluminum in the Animas.

In the post event samples, concentrations of aluminum and all the metals were generally lower although there were storms and such represented in this who Animas concoction. Post event, concentrations of other metals generally were much lower than usual for that level of aluminum. Post event water quality will be explored in Chapter 7.

The correlation of trace metals to aluminum and iron was useful for detecting the plume where it was difficult to distinguish from relatively high concentrations of background metals. This technique maximized use of the abundant metals data, including historic, that rarely has associated sediment data. The technique could prove helpful for future monitoring in the rivers. Importantly, compilation of historical data shows that the concentration of metals observed in the San Juan River during and after the Gold King Mine had elevated concentrations of lead and arsenic for some distance downstream. It also showed that concentrations were within the normal range of variability and comparable or greater concentrations can be expected with stormflow that elevates sediment loads.

CHAPTER 6: MASS TRANSPORT AND DEPOSITION OF METALS

The Gold King release included metals in dissolved form from the mine effluent, particulate metals entrained as sediment by the flood wave, and colloidal aluminum and iron oxide solids that formed as the acidity of the Animas River neutralized the plume of acidic mine water. High concentrations of total and dissolved metals decreased as the plume travelled through the system. Reduction in concentrations occurred partly due to dilution and geochemical reactions that transformed metals from dissolved to solid forms. These processes had no impact on the mass of metals transported in the system. Concentrations of metals in colloidal/particulate form was reduced as particles settled from the water and deposited in the streambed.

In this section, we trace the transport and fate of the released metal mass including deposition of the mass as the plume traveled through the Animas and San Juan Rivers. This material was of concern for effects on aquatic and terrestrial biota and for potential future release back into the water in high flow events.

Methods. The empirical model and WASP produced traces of metal concentrations through time as the Gold King plume passed modeled locations (see Chapter 3). The metals concentrations were translated to mass by multiplying the concentration of metals by flow volume in each time period determined at or calibrated to the USGS gage and summing for the duration of the plume.

$$\sum_{1}^{n} Concentration \left(\frac{mg}{L}\right) x \frac{Q(liters)}{1{,}000{,}000} = Load\ (kg)$$

where n = number of time steps and Q is the USGS reported flow for each 15-min period at the gages used by the empirical model and estimated for each time period by WASP for individual segments. The calculation is visualized in Fig. 6-1.

Figure 6-1.

Although the empirical model and WASP were initialized at the same concentration at the Cement Creek gage and were calibrated to the total load at 12 locations, the two models were not expected to agree on mass transported by each site due to differences in methods that varied in determining the duration, peak concentration, the plume “shape”. WASP loads represent the 99% of the plume mass. The empirical model generally had shorter duration plumes and was ended when the total concentration declined close to pre-event estimated or observed concentrations which captured 95% of the mass.

It should be clear from the superposition of the empirical and WASP estimated plumes that the two models will not estimate the same mass load from the plume (Fig 6-1). While the peak concentration is similar in this case, WASP has a much longer duration and extended period of much higher concentrations than observed. Thus it is likely to overestimate the plume mass. WASP probably overestimates the concentrations on the leading edge due to numerical dispersion. However, relative to the observations included in Fig 6-1, it may also overestimate on the falling limb of the plume.

Metals Mass Transport By the Gold King Plume

The particle characteristics of metals input to river system from the Gold King release varied depending on source and changed as the plume travelled through the system. Metals from the mine pool were dissolved ions that formed into amorphous solid unaggregated colloids and aggregated precipitates as the plume neutralized as it travelled (Fig 5-2). Material entrained from the waste pile or within the stream as the moderate-sized flood wave passed were likely a mixture of inert and contaminated minerals formed in place or attached to clays and sediments. Thus, the metals mass in the plume likely had a range of particle size and suspension characteristics that would influence their transport and potential for deposition within the river system.

Figure 6-2. Particle characteristics.

The transport of total metals in the Animas and San Juan Rivers determined from WASP and Empirical modeling is shown in Fig. 6-2. Both models were initiated with the estimate of mass delivered from Cement Creek (see Chapter 3). Metals mass declined as the Gold King plume traveled through the length of the Animas and San Juan Rivers. Metals concentration in the water column declined with dilution from incoming water, as discussed in Chapter 5. However, the decline in mass of colloidal/particulate materials could only occur through deposition.

Animas River Plume Mass. A significant mass of metals was gained in Cement Creek as the plume moved from the mine to the outlet of Cement Creek in Silverton (Chapter 3). Approximately 490,000 kg of primarily colloidal/particulate mass was input from Cement Creek to the Animas River. Gold King metals mass declined sharply as the plume moved through headwaters of the Animas River. Mass at the empirically modeled locations is shown in Fig. 6-3. Metals mass declined sharply, with most of the mass lost from the water column in the upper and middle Animas River between Silverton and Durango (Fig. 6-3). The total fraction input to the Animas River from Cement Creek was predominantly colloidal/particulates as well as 15,000 kg of dissolved metal ions. All of the dissolved mass was transformed to colloidal/particulate mass through formation of iron and aluminum oxides within this section as well (Chapter 5).

Figure 6-3.

Both models shown similar patterns of decline in mass transported. However, the empirical model suggests that the plume lost more mass in the canyon reach of the Animas in the San Juan National Forest between Silverton (RK 16.4) and Bakers Bridge (RK 64) than WASP estimated. WASP loses more mass between Baker's Bridge and Durango (RK 94). In addition, WASP maintains about twice as much mass through the lower Animas and San Juan than the empirical model (Fig. 6-3). Differences occur because WASP sums mass over a longer duration than the empirical model that reflects observed concentrations only (discussed in Chapter 4). Thus, uncertainties in estimating plume concentration and duration are represented in the range of mass between the two models shown in Fig 6-3.

The Gold King summed metals mass transported through the Animas River as determined by the empirical model is shown in Figure 6-4. The empirical model suggests that 85% of the metals introduced to the Animas at Silverton were deposited by the time the plume passed through Durango and 90% were deposited before the plume entered the San Juan River. The mass of arsenic, lead, copper and zinc transported through the Animas River are shown in Fig. 6-5. The individual metals follow the same overall pattern as the summed metals, with most of the load deposited within the upper Animas through Durango. Zinc mass declined more slowly but was reduced by 70% by Farmington.

Figure 6-4.

Figure 6-5.

Within the Animas River, the metals mass transported during the Gold King Plume was derived almost exclusively from the release. Exceptions would include the major cations (Ca, K, Mg, Na), barium, and selenium that gained mass as the plume moved through the Animas, presumably from other sources.

San Juan River Plume Mass. The profile of metals mass in transport changed significantly as the Gold King plume passed from the Animas into the San Juan River. At the time of the Gold King plume, the San Juan was carrying a high load of sediment that had a natural concentration of metals. Chapter 5 discussed the relationship between metals and sediment, using the natural composition of aluminum and iron as dominant metals associated with soils and sediments as a correlating variable for identifying the trace metals carried within the plume.

The large amount of sediment in the San Juan River essentially equalized the concentration of many of the minor metals carried in the Gold King plume. This is also illustrated in the mass of metals computed for the duration of the plume for the Animas and the San Juan Rivers. Fig. 6-6 shows the mass of metals in the Animas, and the estimated mass in the San Juan River above its confluence with the San Juan. To estimate the upstream load, the Animas at RK 190.2 plume load is subtracted from the load in the San Juan at RK 193 computed for the same length of time.

Figure 6-6. Comparing metals mass for Animas and San Juan at confluence.

There is a large background mass of many of the metals in the San Juan River during the passage of the Gold King Plume, especially iron and aluminum. Because other metals are strongly correlated with these two metals that are a major component of soils and sediment, the mass of most elements was also elevated, and generally present in higher concentrations during the plume. Metals such as beryllium, cobalt, nickel and vanadium were present in much higher concentrations in the San Juan, yielding much greater mass than the plume. However, the plume was highly enriched in lead (as discussed in Chapter 5), which resulted in a load of approximately 400 kg that was distinctly in excess of what the San Juan River would normally carry during similar sized flow events (Fig. 6-6). The mass of zinc, arsenic, and copper were elevated in the plume but roughly comparable to the mass carried in the San Juan River at the time the plume moved through.

The background sediment and metals load mask the passage of the Gold King plume through the length of the San Juan River as sediment loads in the river increased (Fig. 5-16). The plume mass estimated by the empirical model for San Juan locations is shown with the background mass for the same time period in Fig. 6-7.

Figure 6-7. Gold King plume mass in the San Juan River.

Plume mass in the San Juan River estimated by the empirical model was about 44,000 kg at Farmington, declining to approximately 24,000 kg at Mexican Hat. Aluminum and iron mass continued to increase significantly in the lower reach of the river before joining Lake Powell. Lead declined somewhat through the San Juan, while copper increased from initial levels in Farmington.

Plume Mass Delivered to Lake Powell. The San Juan River enters Lake Powell approximately 548 kilometers river distance from the Gold King mine. Both the empirical and WASP model stopped modeling at RK 510 because there were few samples to calibrate the models and those that were available were unable to detect the plume. Extending the rate of decline observed in each modeling approach for the final 50 km, suggests that between 18,000 kg (empirical) and 56,000 kg (WASP) of metals were delivered to Lake Powell by the Gold King plume over a 2-day period arriving early August 13. The Gold King plume metals were mixed with at least 490,000 kg of background metals commonly transported during moderate flows in the San Juan River.

Deposition of Gold King Plume Metals

Loss of mass as the Gold King plume flowed down the Animas and San Juan Rivers means that material was transferred to the bed of the rivers. The section focuses on settling of the material within the rivers. The deposited material was a varied mix of particles, colloids, and minerals that would have varied spatially within the rivers, both laterally and longitudinally. Fig. 6-8 shows various forms of deposited mass observed in the rivers, including sludge-like deposits on the channel margin, sediments deposited onto the streambed, strand lines of colloidal material painted onto rocks in the stream, and aggregated colloids that settled in slow velocity areas.

Figure 6-8.

Modeling suggests that most of the Gold King plume mass deposited within the upper Animas River below Silverton to Durango. The estimated mass deposited between locations is shown in Fig. 6-9. Both models agree that much of the Gold King plume mass was deposited between Silverton and Durango. The empirical model distributes the mass more evenly through the entire length, including within the steeper canyon in the San Juan National Forest. WASP maintains transport of particles through this steep, confined channel, and deposits more of the material in the braided and meandering reaches between Baker's Bridge and Durango.

After initially high rate of deposition upon entering the Animas River at Silverton, the general rate of decline predicted by WASP was between 1000-2000 kg per kilometer of river length between Silverton and Aztec, NM with a 10-fold increase in the reach between Baker's Bridge and Durango (Figure 6-9B). WASP also predicted a higher rates of deposition at the confluence of the Animas and San Juan and at confluences of other major tributaries as they joined.

Figure 6-9. Mass deposited by reach,

Figures 6-10 through 6-13 provide photos of reaches of the Animas before (2014) and after passage of the plume (October 2015) from GoogleEarth imagery. Ground-level photographs are also provided in Figure 6-14. These sequence of photographs show that metals mass settled within the stream in slower areas along the channel edges and behind obstructions. Within the braided reaches below Silverton and Baker's Bridge, relatively higher flow during the plume had occupied side channels. As flow receded, deposits of yellowboy were left outside the active channel where they would dry and potentially be remobilized in subsequent high flows. In the meandering reach near Durango (Fig. 6-13) sludge like deposits were left at the high water mark along the channel banks. Most of the Gold King mass was probably left in the slow velocity areas along the channel margins near the banks.

Figure 6-10.

Figure 6-11.

Figure 6-12

Figure 6-13.

Figure 6-14.

Composition of deposited material. Masses of minerals precipitated from the release waters as they intermingled and reacted with Animas River water. These minerals could be estimated from thermodynamic modeling of titration of "Plume + Background Mean" water with calcite alkalinity that is present in the Animas (Fig. 6-15). Cations initially in alunite and jarosite likely will ultimately enter the more stable gibbsite and ferrihydrite phases, respectively. Whether low trace levels of Ba and Cu will form discrete mineral phases such as barite and tenorite, respectively, or sorb to and isomorphically substitute directly in more stable mineral phases is uncertain, but ultimately these ions likely will be bound to more stable minerals and their aqueous concentrations maintained at low levels as suggested by modeling described in Appendix C. Nontronite is a commonly occurring smectite clay mineral. Gibbsite, ferrihydrite and birnessite are commonly occurring oxyoxide minerals and likely will recrystallize to similar, but still more stable, phases over time. See Appendix C for more discussion of the geochemistry of the Gold King plume and precipitated material that were deposited.

Figure 6-15.

When minerals precipitate from solution, more soluble mineral phases generally are the first to precipitate for a combination of thermodynamic and kinetic reasons (Steefel and van Cappellen 1990). Post plume adjustments to these deposits over time should be expected. Large quantities of incipient amorphous Fe and Al minerals formed in the Gold King plume. As they formed in suspension, some remained in suspension and some settled and adhered/cohered to the river bottom. Over time, these less stable incipient phases recrystallize to more stable phases. For Fe, a mineral ripening sequence might be amorphous Fe(OH)3, short-range ordered ferrihydrite, ferrihydrite, and then goethite (or hematite; in detail goethite might form directly from ferrihydrite or by dissolution and reprecipitation). For Al, the sequence might be amorphous Al(OH)3, microcrystalline gibbsite, then gibbsite. Where the river bottom is dominated with incipient phases, the water will tend to have higher solution concentrations. Alternatively, if the river bottom is dominated by stable oxides, the stable oxides act as a sink for any elevated metals the water receives from dissolution of the incipient phases. In both upriver and downriver, there will be a net transfer of metals from incipient phases to stable.

Gold King Mine Deposit Effects on Concentrations of Metals in Streambed Sediments

Metals deposited as oxides and other incipient minerals during passage of the Gold King plume were incorporated into the streambed sediments. Concentrations were quantified by collecting the top layers of the streambed or deposition layers and processed for metals content. Many of the post-event samples were biased towards deposits such as those shown in Figures 6-11 through 6-14. The general pattern of metals mass in the river sediments after the Gold King event for the length of the Animas and San Juan Rivers is shown as the statistical distribution of samples collected after the release in Figure 6-16. The concentration shown is the average of samples collected at sampling locations in the 2 months following the event. The mass of 5 metals per unit block of sediment was determined by multiplying concentration expressed as mg/kg by the estimated weight considering bulk density of the top 5 cm of the streambed.

Figure 6-16. Bed sediment composition after the event through whole system.

There is a strongly declining trend in metals mass in the sediment through the Animas River with high variability among samples. Metal mass in the bed of the San Juan River are very low with relatively small variability among samples and along the length of the river. Metals are a natural component of soils and are expected to be in river sediments in proportion to their natural occurrence. Metals naturally occur within soils and sediment. Shown on the right side of figure is the range of metal concentration sampled in natural surficial deposits and soils of the western United States in a synoptic survey of the western United States by Shacklette *et al.* (1984) to provide perspective on the metals metals carried in these two rivers. Metal concentrations within the headwaters of the Animas River equal or exceed the highest metals concentrations while those in the San Juan River are very low relative to the observed range.

The WASP water quality model simulated the transferral of mass to the streambed and computed the effect on sediment metals concentrations (Fig. 6-17). The general pattern of deposition predicted by WASP was similar to that observed in sediment samples. WASP predicted differential effects on metals composition in the sediment reflecting variability in the flow and depositional potential within the rivers. Geomorphic controls on river flow were especially important in the Animas River as the Gold King plume carried a large mass of metals in flow that alternately accelerated and decelerated with valley conditions.

Figure 6-17.

Sediment metal concentration for 4 metals from samples collected throughout the Animas and San Juan Rivers after the Gold King plume are shown Fig. 6-18. Also shown are sediment concentration data collected in years prior by the USGS at gaging stations, by EPA to support mine remediation activities in the Animas headwaters, and in the USGS synoptic survey of sediments in the Animas reported in Church *et al.* (1997). The post-event samples show wide variability among samples, possibly reflecting the variability in depositional environments sampled. The earlier samples document the same pattern of decrease in metals concentrations in the Animas River from very high concentrations in the headwaters to relatively low concentrations near Farmington and generally low concentrations in the San Juan River that vary little along its length. Church *et al.* (1997) concluded that metals from mining impacts in the headwaters and at downstream processing facilities continue to contaminate the Animas River through much of its length from both ongoing and historic input of acid mine drainage into the river. Generally, metals concentrations observed in the Animas and San Juan Rivers after passage of the Gold King plume were within the historic range of variability. We will examine these patterns in greater detail.

Figure 6-18.

Animas River Bed Sediment. Sediment concentrations of lead, arsenic, copper and zinc in the Animas River are shown for post Gold King and USGS pre-event samples in Fig 6-19. Also shown is the WASP estimate of bed concentrations, where the predicted deposited concentration is added to a baseline estimated by fitting a regression to the USGS data. This may underestimate more recent bed concentrations in the Silverton area as AMD effects have increased since 1996 after much of the USGS data was collected.

Figure 6-19.

Post-event concentrations of the four metals (and others not shown) generally increased in the river segments identified by WASP as likely depositional zones and generally near the predicted level. We note that the empirical model estimated greater deposition within the reach between river kilometer 16.4 (A72) and 64 (Bakers Bridge), but no samples were collected in this remote and difficult to access reach of river. While there was a wide range of variability in the post event samples, at least some were significantly larger than the estimated baseline and within the magnitude suggested by WASP. A relatively large increase predicted from RK 120 to 130 was not observed.

Water and sediment concentrations will be further compared to pre-event data to analyze post release changes to the rivers in Chapter 8 where statistical comparisons of data shown in Fig. 6-18 will be performed. While metals carried in the Animas River water during the passage of the Gold King plume were almost exclusively attributable to the release, the metals in the streambed after the plume passed also strongly reflected the history of metals contamination in the watershed. Church *et al.*

(2007) noted that millions of tons of ore and mine waste were dumped into the Animas in multiple locations and that those sediments continue to contaminate the streambed along with ongoing AMD. Lack of significant change to sediment concentrations where historic data were available may reflect the existing contamination.

The recent deposition from the Gold King release can be compared to the pre-existing mass of metals in the streambed by translating metals concentrations in the streambed to mass, similar to what was done to produce Figure 6-20. Concentration is translated to mass with a sediment bulk density and the deposited mass (e.g. Fig. 6-20B) is spread over the length of each reach (Table 6-3). The Gold King release contributed a substantial mass of sediment to the Animas River in the vicinity of Silverton, increasing the mass already in the streambed by 54%. Downstream of the Silverton, mass from the Gold King increased by 2-3%. This relatively small mass would be difficult to detect given the variability in samples.

Table 6-1.

The summed metals mass in a unit area of stream before and after passage of the Gold King plume is shown in Fig. 6-20. Background metals mass ranges from 3 to 6 kg/m2 (assuming 5 cm depth). The mass added in the Silverton area was 3.3 kg/m^2 in Silverton but between 0.1 and 0.2 kg/m^2 in segments downstream.

Figure 6-20. Deposition in kg/m^2 in 3 upper reaches.

San Juan Bed Sediment. In contrast to the Animas River, bed sediments in the San Juan River have low concentrations of metals. Post Gold King plume concentrations of 4 metals are shown in Fig. 6-21. Bed concentrations were within historical levels relative to the few data available from USGS data gage sites. The riverbed has been extensively sampling since the Gold King release. Metals concentrations are low and relative uniform through nearly 350 km of river. Metals concentrations are variable at individual sites, but are generally lower than observed at USGS gages, especially in the lower reaches of the river after Four Corners, UT. Metals concentrations in the San Juan River are in general low relative to surficial deposits sampled throughout the western United States as reported in Shacklette et al. 1984. The predicted concentration with deposition from WASP generally exceeds observed lead but is within the range of variation for the copper, arsenic and zinc.

Metals concentrations measured in the river during high flow events were shown in Chapter 5 to be relatively high and water quality criteria for some metals are often exceeded (Chapter 7). This does not occur because the metals concentrations are high in the bed of the river, but rather because a large quantity of sediment with naturally low concentrations of trace and major metals is transported in the San Juan River during high flow, eventually exceeding the criteria. Historic records of sediment in transport have recorded suspended sediment concentration as high as 330,000 mg/l in the San Juan River. Sediment concentration was about 2,000 mg/L during the Gold King release and higher in subsequent storm events.

Figure 6-21.

Lake Powell Bed Sediment. The San Juan River flows into Lake Powell at approximately 548 km distance from the Gold King Mine. Modeling suggests that during the Gold King plume, about 430,000 kg of metals flowed into Lake Powell, of which between 18,000 kg (empirical model) and 56,000 kg (WASP) was from plume. The metals in the plume and the background sediment mass were the same.

Figure 6-22. Photographs

Concentrations of metals in lake sediments have been determined in the past by coring (USGS 2014). Following the spill, sediment traps were deployed by USGS in August 2015 at the terminus of the San Juan River in Lake Powell to assess recent and ongoing deposition and sediment metal concentrations (Utah DEQ 2016). The traps capture sediment as it falls to the bottom of the reservoir. Traps were retrieved in November 2015 but results have not yet been reported.

The bed sediment composition of the river after passage of the Gold King plume averaged from Montezuma to Bluff is low in metals concentrations relative to the 2014 lake core samples (Fig. 6-23). If Gold King plume metals deposited in the bed of the San Juan, they were not at concentrations that would affect the Lake based on the streambed samples. If the 18,000 to 56,000 kg of metals travelled to the lake without much settling in the river they could elevate the concentration more than seen generally along the San Juan River although Gold King plume metals were substantially diluted with natural river sediments.

Figure 6-23.

Annual Background and Post GKM Metals Load -- Animas River

The Gold King release resulted in significant deposition of metals mass in the Animas River, especially in the upper reaches from Silverton to Durango where 90% of the metals (450,000 kg) settled as colloidal/particulates. This material was visibly evident as yellow deposits of aggregated colloids, sludge, and particulates. At the same time, streambed sediments in this reach of the river have historic and ongoing contamination from mine waste and acid mine drainage from economic mining in the region for over a century. To place this mass of material in context, we develop a simple model of daily and annual metal load at two locations where sufficient pre-event data was available.

Total and dissolved metals have been measured at Silverton and Durango for a variety of studies, including the USGS Animas River acid mine drainage study (Church *et al.* 2007) and EPA studies in support of acid mine drainage remediation. Metals concentration as a function of streamflow for six dissolved metals important in the Gold King release at Durango is shown in Fig. 6-24. Spring snowmelt data from 2016 is also shown on the graphs although these data were not included in the regression relationships shown with each metal. The historic data were collected over a range of flow up to 2,900 cfs, (82 m^3/s) which is about equal to the long term average peak discharge during snowmelt. Streamflow peaked at 5,110 cfs (145 m^3/s) on June 6, 2016. Five samples were collected during the 16 days when streamflow exceeded the average peak, thus expanding the high flow sampling record in Durango significantly.

Figure 6-24. Examples of dissolved metals at Durango

Dissolved metals such as iron and aluminum are strongly associated with the streambed and tend to increase with flow. Dissolved iron, especially, was far above any previously measured values during 2016 snowmelt, as was aluminum for part of the period. Changes in metals concentrations in the year following the Gold King Mine release will be discussed in detail in Chapter 8. Similar data is available for additional metals at Durango and Silverton in Appendix F where the annual metals loading model is documented.

Other dissolved metals tend to decrease with flow, probably through dilution during high flow with incoming fresh water. We note that the range of concentration of dissolved metals is not large over a wide range in flow, but it will produce some annual variability.

Colloidal/particulate metals (computed as Total Recoverable – Dissolved) tend to increase with flow. Presumably this occurs as they are entrained as or with particles during flow events sufficient to mobilize sediment. In the Animas River at Durango, there is a marked increase in all of the metals when streamflow exceeds approximately 1,600 cfs (45 m^3/s).

Figure 6-25. Examples of colloidal metals at Durango

To estimate annual metals load, we multiply daily flow volume times concentrations determined from these concentration relationships (see Appendix F for additional metals and description of the method). To estimate background loads, the daily flow is the long term average for the day of year for the period of record available as a station statistic provided by the USGS. Because the annual flow hydrograph is dominated by snowmelt, the long term average flow primarily reflects this source of runoff. Combining the discharge with the metals concentration regressions produces an annual pattern of concentration and loading like that shown in Fig. 6-26 for zinc. A similar modeling approach to estimating metals concentrations and potential toxicity was applied by Besser and Leib to (2007) the upper Animas near Silverton. These relationships for aluminum, iron, manganese, lead, copper, and cadmium are provided in Appendix F. The daily concentration models will also be used to estimate bioaccumulation in Chapter 7 and relationships between concentrations and flow will be used in statistical analysis of post event water quality in Chapter 8.

Figure 6-26.

The Gold King plume load can be put into context relating to the metals mass typically carried on a daily and annual basis at Durango using the annual concentration model based on regressions of concentration with flow. Table 6-2 provides the annual mass of seven metals carried over the course of an average year at Durango. The Gold King plume increased the annual load of metals by about 1%. The effect was more significant for particulate lead and iron that were increased by 5.4 and 4.7% respectively.

Table 6-2. Annual mass load at Durango.

On a daily basis, the Gold King plume carried particulate metals mass about equal to 1 to 2 days of spring snowmelt, varying with metal and the dissolved mass was general less than a day of snowmelt. Notably greater was particulate iron and dissolved manganese. Of course, the Gold King plume occurred during relatively low flow conditions and concentrations and mass were significantly elevated above what would be normal for that level of flow.

Table 6-3.

Resuspension of Gold King Metals in Snowmelt

A large mass of metals was deposited in the Animas River as the Gold King plume moved through, much of it between Silverton and Durango. The first high flows that could have mobilized this material from the streambed of the Animas upstream of Durango occurred during spring snowmelt from May to June 2016. We combine WASP and daily empirical modeling just described to evaluate the mobilization of Gold King deposits in the upper Animas River.

Four resuspension simulations were performed with WASP selecting days that covered a range of moderate to high flows. Flow measured in 2011 was used as the record was complete for the entire Animas and San Juan system. This simulation required sufficiently high flows to mobilize sediments, not necessarily an accurate flow record from 2016 which were not yet available.) Gold King deposits could be mobilized at any of the flows but, like sediment, would most likely be entrained during the highest flows.

WASP resuspended material according to the same particle and hydraulics criteria calibrated to model deposition during the plume (See Appendix B.) The Gold King plume deposits were an atypical mixture of aggregated and unaggregated colloidal/particulates compared to inert particles normally modeled. There is uncertainty in these model simulations due to the unknowns concerning the variable nature and properties of Gold King plume deposits that had weathered in place for nearly 10 months. In this simulation, WASP resuspended all of the deposited materials at once and put them into water that had no metals, so the concentrations would be in addition to the background concentrations that would normally be observed.

Resuspension simulations for total metals is shown in Fig. 6.27. WASP predicted virtually no metal deposition in the San Juan River from 200 km to 550 km during the plume and so virtually no remobilization is simulated there. The resuspended deposits have different concentrations depending on flow. Since the entire deposit is remobilized at once, the lower the simulated flow the higher the concentration. The simulated concentrations at all flows are small. At Silverton they range from a low of 0.0002 mg/L at high flow to 0.002 mg/L at low flows. The most realistic simulations are for the mid to high flow range for a scenario of complete remobilization at once. This small concentration would probably be difficult to detect within the normal concentrations in the river at these flows. Estimated resuspended concentrations for 4 metals are shown in Figure 6-28. The predicted remobilization concentrations of individual were very small (copper 0.0015 mg/l; lead 0.01 mg/L; zinc 0.0002 mg/L).

Figure 6-27.

Figure 6-28

To assess transport of the Gold King deposited mass during snowmelt, we used the daily flow/concentration regressions to estimate the daily metals load as described in the previous section. The expected annual load from October 2015 through the spring snowmelt season of 2016 was determined based on the regressions using only historic samples to represent background annual metals load (e.g. Fig 6-26). We then updated the regressions with samples collected from April – June 2016. (Those samples are also shown in Fig 6-25.) Many of the 2016 samples were collected at higher flow than had been sampled previously. Some metals appeared elevated, as will be discussed further in Chapter 8. The daily mass was then computed with the 2016 regression but using the average long-term average flow rather than 2016 observed flow to focus on the importance of the sample concentrations rather than the flow effects. Results are shown in Fig. 6-29.

Figure 6-29.

The daily metal concentration from the flow regression equations for copper, lead and zinc for the average (background) year and 2016 are plotted in Fig. 6-29. For example, these are shown for particulate zinc at Durango in Fig 6-29. Background concentrations of particulate zinc at Durango during the peak of spring snowmelt is normally about 0.15 mg/l and 0.03 mg/l at low flows at the start of spring snowmelt. WASP predicts that the concentration from Gold King deposits would range from .013 mg/L at the lowest flow to .001 mg/L at the peak. There were small differences in concentration at the peak based on 2016 sampling that are in the range predicted by WASP.

The relative increase in concentration during the peak flows shows the relative effect of the 2016 samples on high flow metals concentrations. The difference between the background concentration and 2016 at the peak is small, but it is similar to the range predicted by WASP. These small differences accounts for the increased metals mass in Fig. 6-30.

The difference between the two traces is taken as the mobilization of Gold King deposits. The excess mass was determined by calculating the load integrated over time and subtracting the background mass from the 2016 mass. The excess mass for 7 metals is shown in (Fig. 6-30) compared to the mass of metals deposited within the Animas River between Silverton and Durango during the Gold King plume. For example, about 25,000 kg of colloidal/particulate aluminum was deposited during Gold King and approximately 38,000 kg of additional aluminum was transported in 2016. About one half of the iron and one third of the deposited lead may have been transported in 2016. Flow was much greater than average at the peak of snowmelt in 2016. If the 2016 flow was used for the calculation, the excess aluminum and lead would have been closer to 70% deposited. This analysis suggests that a mass of metals equal to or greater than the mass deposited from the Gold King plume was transported out of the upper Animas during snowmelt. While a large mass was removed it was transported at low concentrations.

Figure 6-30

Spring snowmelt was the first time after the Gold King plume that the upper Animas region experienced large flows. The lower Animas River experienced a significant large storm on August 27, 2015 comparable to snowmelt just weeks after the Gold King release (Fig 6-31). . The storm did not affect the Animas above Durango. Gold King metals deposited in the lower Animas could have been suspended and moved out in the August 2015 event. Only one sample was collected late in the storm during that event. Eve holding the observed sample concentrations constant over the hydrograph, the metals mass carried in that storm far exceeded what was transported or deposited during Gold King. It was likely that this monsoonal storm had some effect on the Gold King deposited mass.

Figure 6-31.

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CHAPTER 7: POTENTIAL EXPOSURE TO METALS CONTAMINANTS DURING THE GOLD KING PLUME

Potential exposure of humans and terrestrial and aquatic life to metals following the Gold King Mine incident were reasonably short-term in nature (hours not days) and were characterized by an initial spike in concentrations in the water that dissipated rapidly returning to pre-spill conditions. Emergency response managed by EPA and the states and tribes limited human-related exposure by curtailing use of the Animas and San Juan Rivers for drinking water, irrigation, livestock watering and recreation. Concerns remain for delayed contamination with potential remobilization of the deposited metals throughout the river system.

For fish and wildlife, exposure to metals could not be managed. It is well established that fish and other aquatic biota readily bioaccumulate metals from their surrounding water, sediments, and food. Such bioaccumulated metals can represent significant toxicological threats not only to exposed aquatic organisms but also to terrestrial wildlife and humans which that consume contaminated fish or aquatic invertebrates. Initial impacts to organisms during the plume would likely have been acute in nature due to the initial pulse exposure. Subsequent effects could occur from chronic exposures to metals sequestered in the streambed. The Animas River has a history of such contamination to which the Gold King Release added fresh material.

States and tribes have adopted water quality criteria or standards that establish maximum concentrations of constituents, including metals, in water or sediments to protect the beneficial uses of water. Criteria vary according to uses including water supply, agricultural and livestock, recreational activities and habitat for terrestrial and aquatic life. Numeric criteria reflect assumptions of effects mechanisms such as ingestion or dermal contract coupled with magnitude and duration of exposure. There are criteria to protect aquatic habitat for acute exposures reflecting high concentrations for a short period (typically concentration not to exceed for 96-hours) while chronic exposure criteria assume low concentrations for extended periods (typically 30-day average).

EPA has recommended criteria for many of the beneficial uses. States and tribes in the area affected by Gold King have adopted metals criteria for individual metals. Metals criteria variously specify dissolved or total fractions for specific uses. Some criteria are a single threshold value while others are varied by hardness of the water. Criteria assigned to specific river reaches vary by designated beneficial uses. Some criteria are similar between states and tribes for the same beneficial use but many differ. A list of metals criteria relevant to the area affected by the Gold King plume categorized by water uses are compiled in Table 7-1.

Gold King Plume Relative to Water Quality Criteria

Potential exposure to metals in the Animas and San Juan Rivers was performed by screening measured and modeled data relative to the water quality criteria. We assess potential exposure during the passage of the Gold King plume at locations where the plume concentrations were modeled empirically and using WASP.

Methods

The Gold King plume was assessed by comparing the modeled metals concentrations for each metal in each time step to the appropriate criteria and counting the hours that a criteria was exceeded. The plume passed as rise and fall of concentration with a fairly limited time period, so duration of exposure would have been sequential. Typically state or tribal criteria appropriate to the location of the site were applied. Due to differences in criteria between states, there can be abrupt changes along the route of the plume as it moved through three states. We fill in with EPA criteria for recreational contact because EPA screened with this criteria during the plume. UDEQ applied its own recreational value to portion so the San Juan River in Utah. An extensive length of the San Juan River flows within the Navajo reservation. The Navajo Nation Environmental Protection Agency (NNEPA) has a complete set of criteria for metals. We provide a specific accounting at San Juan Sites relative to these criteria.

Hardness criteria were calculated for all sites 185 mg/l. Hardness measures during the passage of the plume were limited. Samples collected by NMED in the lower Animas on August 8 ranged from 180 to 200 averaging 184 mg/L. Hardness of 185 was applied to the entire Animas River during the plume. Hardness sampled in the San Juan in Farmington during the same period ranged from 190 to 230 averaging 212 mg/L. This value was used for sites in New Mexico. The lower the hardness, the lower the criteria, so we opted to apply to the lower value. Utah DEQ has published similar comparisons of water samples to their state criteria for San Juan water samples so we apply the same criteria. Assignment of criteria was also attentive to designated beneficial uses at the reach scale. This was important in the upper Animas where Cement Creek has no designated uses and the Animas near Silverton has very limited uses.

Given the relatively short temporal period of the plume, the aquatic acute criteria are the most relevant for evaluating the immediate potential impact of the plume on aquatic life. Note that we provide the hours criteria were exceeded. We do not apply any time duration assumptions. Other uses including domestic supply and agricultural consumption and recreational uses of the Animas and San Juan Rivers were curtailed for several days during and after passage of the plume.

Table 7-1. Table of compiled criteria.

Concentrations Relative to WQ Criteria in Surface Water During the Gold King Plume Based on Modeling

The number of hours that criteria were exceeded for each metal at each of the empirically modeled locations as the Gold King plume passed are provided by water use category in Tables 7-2 through 7-7. The WASP generated simulations for lead, arsenic, zinc, and copper were also screened for water quality exceedances. Results were very similar to those for the empirically modeled plumes. WASP hour counts are provided in Appendix G.

Table 7-2. Recreational criteria exceedances

Table 7-3 Agricultural criteria exceedances

Table 7-4 Aquatic acute criteria exceedances

Table 7-5 Navajo Nation criteria exceedances

Table 7-6 Ute Mtn Ute criteria exceedances

Table 7-7 Recreational criteria exceedances

Given the high concentration of virtually all metals as the Gold King plume entered the Animas River, and the subsequent dilution and deposition of colloidal/particulates in the upper Animas River, exceedances of water quality criteria attributable to the Gold King release were expected to be greatest in this section of the river. Note that Cement Creek had high concentrations of metals that exceeded most criteria, but since it has no designated beneficial uses, it had no exceedances. The count of hours in the Animas below Silverton to RK 16.4 are included even though this reach also has limited assigned uses.

Hours exceeding criteria generally declined with distance for all beneficial uses and metals through the length of the Animas River. Recreation criteria for several metals was exceeded at Silverton only (Table 7-2). Criteria related to agriculture, irrigation and livestock for several metals including arsenic, copper, lead, and manganese were exceeded for a number of hours as far downstream as river kilometer 132 on the SUIT reservation (Table 7-3).Domestic supply criteria were very similar to agricultural at Colorado sites.

Exposure length for acute effects is generally taken as 96-hours, except in Utah where duration is one-day. Aquatic acute criteria for aluminum mostly reference total recoverable metals except in Utah where dissolved criteria are applied (Table 7-1). Chronic aquatic criteria concentration values are lower than acute criteria as these criteria reflect prolonged exposure (generally 30 days but varying among states and tribes: the exception of Utah and Ute Mountain Ute tribe that applies a 4-day criteria). Chronic criteria for Colorado and New Mexico designate dissolved concentrations for most metals, except for aluminum which are applied as total recoverable (see Table 7-1 for specific metals).

Exceedence of aquatic acute criteria was uncommon (Table 7-4). One prominent exception was aluminum for which criteria were exceeded for most of the length of the Animas and San Juan Rivers. Iron and aluminum oxides were among the major components of the yellowboy in the plume. Aluminum concentrations had declined below criteria in the Animas at Farmington, but increased significantly after joining the San Juan River that was carrying high concentrations of sediment that also elevates aluminum and iron (see Chapter 5). Iron was also prevalent in the plume but has relatively few assigned criteria so the plume did not trigger many exceedances.

The Mountain Studies Institute monitored water quality during the plume in Durango (Mountain Studies Institute 2016). They also reported that aquatic criteria for aluminum were exceeded at the peak of the plume and that lead exceeded domestic water supply criteria for a 26-hr period. They noted that fish and benthic macroinvertebrates in the Durango reach of the Animas River largely survived the Gold King release based on reports from the Colorado Parks and Wildlife Department and their own studies. During the period of high lead concentrations, the City of Durango and other public water suppliers had preemptively shut off its intake valve so the city did not receive any drinking water from the Animas River during that time. The EPA Emergency Response Team coordinating local response encouraged private citizens to do so as well.

Chronic criteria were exceeded for a number of metals as far downriver as Durango (river kilometer 94.2) (Table 7-6). Iron has a criteria to protect aquatic life from chronic exposure and it was exceeded for virtually the entire duration of the plume as far as river kilometer 132 near the New Mexico border. Once again, a prominent exception was aluminum, where chronic criteria were exceeded for the entire length of the Animas and San Juan Rivers. As noted, total aluminum concentration significantly increased in the San Juan River with the background sediment.

The Navajo Nation extends along the length of the San Juan River affected by the Gold King Plume. The Navajo Nation Environmental Protection Agency (NNEPA) has adopted water quality criteria for water uses specific to tribal lands (See Table 7-1). NNEPA criteria were applied to all sites on the San Juan River in Table 7-7. Most notable was exceedance of lead for domestic, human contact, and agricultural uses for the river length. Although lead was generally higher with background sediment in the river, correlation analyses discussed in Chapter 5 showed that lead appeared to be elevated above background levels at least as far as Four Corners CO. Aluminum criteria for acute and chronic aquatic life were also exceeded at the time the Gold King plume moved through.

The Ute Mountain Ute Tribe has reservation lands that adjoin the San Juan River between Four Corners ending between Aneth and Bluff UT. The tribe has adopted water quality criteria for this length that corresponds in the water quality assessment tables to Four Corners and Bluff. Water quality screening for these two locations according to tribal criteria is provided in Table 7-8. During the time that the Gold King plume passed these locations, lead, arsenic and aluminum for drinking and ceremonial uses of water, as well as acute aquatic criteria were exceeded for most of the duration of the plume.

The Gold King Mine released a large concentration of many metals into the Animas River at Silverton. Although metals concentrations in the headwaters of the Animas are historically contaminated with metals from mining effects, concentrations were orders of magnitude higher during the passage of the Gold King plume. As the plume travelled, concentrations of dissolved and total metals declined sharply, while duration of the plume increased with flow drag. This pattern was mirrored in water quality criteria exceedances.

However, despite the high initial concentrations, several metals did not exceed criteria for any beneficial use. These included antimony, beryllium, cobalt, nickel, selenium, thallium and vanadium. Exceedances of most of the other metals occurred between Silverton and Bakers Bridge, with some extending as far as river kilometer 132 downstream of Durango Exceedances of aquatic acute criteria were observed for copper, zinc and cadmium for brief periods as far downstream as Bakers Bridge (RK 64). As would be expected, aquatic chronic criteria were exceeded for a longer time and brought in iron and aluminum as well. We note that any criteria based on total recoverable concentrations was more likely to be exceeded than those based on the dissolved fraction.

Reflecting the strongly declining metals concentrations in the lower Animas River, acute criteria for all metals but aluminum were not exceeded after Bakers Bridge (RK 64). The exception was aluminum that exceeded acute criteria through much of the Animas and San Juan Rivers. This criteria is associated with total concentration. New Mexico and Utah water quality criteria were also within criteria in the San Juan River during passage of the plume. Tribal criteria for Navajo and Ute Mountain Ute waters were exceeded for lead and aluminum as their criteria have lower thresholds.

Table 7-8 Summary of lead exceedances

Table 7-9 Summary of aluminum exceedances

The metals that exceeded criteria most frequently were lead and aluminum. To summarize the most frequent exceedances throughout the river system, lead is shown in Table 7-8 and aluminum is shown in Table 7-9. Domestic water and agricultural uses were curtailed throughout the length of river to minimize potential effects. We note that although metals concentrations were largely equal in the San Juan and Animas Rivers as the plume moved, we were able to detect what we interpreted as elevated levels of lead in the San Juan River at least as far as Four Corners, Utah.

Aluminum criteria were also exceeded in a number of locations in the Animas and San Juan Rivers. Most of these exceedances referred to aquatic acute and chronic uses. Aluminum levels were significantly elevated in the Animas River due to the Gold King plume. Aluminum concentrations in the San Juan were elevated partially due to the plume and primarily due to sediments.

The Mountain Studies Institute (2016) has provided a report on metal concentrations during and after the plume at Durango CO. UTAH DEQ (2015) has also periodically published reports on post event water quality sampling for the San Juan River in Utah.

Biological Uptake of Gold King Released Metals in Aquatic Communities

Initial impacts to organisms during passage of the Gold King Mine (GKM) plume would likely have been acute in nature due to the initial pulse exposure. Exposure of fish to acute levels of metals was assessed by comparing plume metal concentrations to acute water quality criteria. For the most part, acute criteria were not exceeded during the plume. Exceptions were aluminum through much of the Animas and parts of the San Juan River, and several hours of excursions above thresholds for arsenic, cadmium, copper, and zinc in the Animas River from Silverton to Bakers Bridge (RK 64). The acute threshold values, however, have inherent assumptions regarding duration of exposure that were generally not met during passage of the GKM plumes. The very high concentrations that characterized the plume lasted for hours but the full plume duration was less than 48 hours and concentrations dropped significantly from peak highs during that time.

Virtually all aquatic biota are known to bioaccumulate metals from their environment. Although some of these metals (e.g., copper and zinc) are essential for the biota's basic metabolic processes and health, other metals (e.g., arsenic, cadmium, and lead) are well known physiological poisons. Even essential metals, however, can be toxic to organisms in high concentrations. Consequently, as part of its integrated assessment of the potential impacts of the GKM release, we assessed whether whole-body metal concentrations in fish could have increased to adverse levels during the passages of the GKM plumes.

There are multiple approaches to estimate the bioaccumulation of metals in aqueous ecosystems. The simplest approaches use bioconcentration or bioaccumulation factors (i.e., BCFs if organisms accumulate the chemical only from water, or BAFs if they accumulate the chemical from both water and food, respectively) to predict chemical concentrations in aquatic biota. These approaches assume that the ratio of an organism's whole-body chemical concentration [$C_o(t)$] to the freely dissolved concentration of that chemical [$C_w(t)$] at any time t is a constant, and that $C_o(t) = C_w(t) \times \text{BAF}$. The accuracy of this approach, however, depends on the organism's rates of growth and of chemical uptake and excretion being significantly faster than the rate of change in the dissolved water concentrations to which they are exposed. If this condition is not satisfied, estimated whole-body concentrations can be very uncertain. Because published BCFs and BAFs for metals are not constants but vary inversely with the prevailing dissolved water concentrations (Chapman et al. 1996, McGeer et al. 2003, DeForest et al. 2007), an alternative kinetic approach was adopted for the GKM bioaccumulation assessment.

To this end, EPA's BASS (Bioaccumulation and Aquatic System Simulator) model (Barber 2008, 2012) was used to predict the expected metal concentrations of Animas River fish under background conditions and immediately before, during, and after the passage of the GKM plume. Unlike the chemical partitioning approaches (i.e., BCFs, BAFs etc.), BASS explicitly models the fish's growth and chemical exchanges between its food, feces, and gill water using a systems of differential equations to simulate the growth, population dynamics, and bioaccumulation dynamics of age-structured fish communities.

Application of BASS

The BASS model was developed to predict the population and bioaccumulation dynamics of age-structured fish assemblages exposed to hydrophobic organic pollutants and class 1B and 2B and borderline metals that complex with sulfhydryl groups (e.g., cadmium, copper, lead, mercury, nickel, silver, and zinc). For its application to the GKM release, the partitioning algorithm which BASS uses to describe the internal distribution of metals, was updated with a hyperbolic isotherm that allows the fish's free sulfhydryl groups to saturate during environmental exposures (e.g., dissolved concentrations at Silverton). BASS was then applied at Silverton and Durango to estimate whole-body metal concentrations of fish during an average flow year prior to the GKM release and during the passage of the GKM plumes..

Because brown and rainbow trout; bluehead, flannelmouth, and white suckers; and mottled sculpins accounted for over 97% of total fish caught during the 2010 and 2012 Southern Ute Indian Tribe (SUIT) fish surveys of the Animas River between Purple Cliffs and the New Mexico Stateline (Zimmerman 2013), EPA assumed that these 6 species would reasonably represented the fish communities at both Silverton and Durango.

BASS's auxiliary parameterization software provides users with complete default data sets of bioenergetic and ecological parameters for 621 species of North American fish; it can also configure a default food web for any combination of these species. This software was used to assign all the bioenergetic, ecological, and morphological parameters required by BASS to simulate whole-body concentrations of cadmium, copper, lead, and zinc at Silverton and Durango under expected background condition and during the GKM plumes.

Daily background dissolved metal concentrations were estimated at Silverton and Durango using the daily concentration model described in Chapter 6, which varies metal concentrations as a function of daily river discharge to produce an annual time series of dissolved metal concentrations that respond to spring snowmelt and other water exchanges. For the GKM plume simulations, hourly dissolved metal concentrations were estimated using EPA's empirical plume characterization model.

Observed metal concentrations in Animas River fishes, which were reported by the Southern Ute Indian Tribe (2015) and by U.S. Bureau of Reclamation (USBR 1996), were used to support model evaluation and comparison.

Annual Simulations of Whole-body Metal Concentrations in Fish

Background whole-body metal concentrations of the fish community were modeled for an average one year time period prior to the GKM release to establish existing metals concentrations in Animas River fishes. These simulations were then compared to the available fish metal concentrations from the middle to lower Animas available reported by the Southern Ute Indian Tribe (2015) and the U.S. Bureau of Reclamation (1996). Although only the most important highlights of these simulations are presented and discussed in the following paragraphs, Appendix E summarizes the full details of these simulations with supporting graphic and tabular results.

Because bioaccumulation dynamics of fish are strongly by their ecology, physiology, and body sizes, the 2-3 year old brown trout was selected as a standard fish to simplify certain aspects of the following discussion. For other aspects of this analysis, however, the entire fish community of concern was used (i.e., all age classes of brown and rainbow trout; bluehead, flannelmouth, and white suckers; and mottled sculpins).

Fig. 7-1 displays the background whole-body metal concentrations simulated by BASS for a 2-3 year old trout at Silverton and Durango. Each of these plots show a rapid initial uptake of metals during the first week of October which is a transient feature of these simulations due to assuming zero initial whole-body concentrations for all fish and metal. Although different in their magnitudes, each plot also shows an identifiable response to the April-July snowmelt. With the exception of copper at Durango (Fig. 7-1b), BASS-simulated whole-body metal concentrations all decease during this period. Whereas the most pronounced decreases were predicted for cadmium, copper, and lead at Silverton, only small decreases were predicted for cadmium, lead, and zinc at Durango.

Figure 7-1. Annual dynamics of background whole-body cadmium

The distributional characteristics of the simulated background whole-body concentrations in all age classes of brown and rainbow trout; bluehead, flannelmouth, and white suckers; and mottled sculpins are displayed in Fig. 7-2 with box plots. The top and bottom of each box corresponds to the first and third quartiles of the data, respectively; the line inside the box is the data's second quartile (i.e., median); and the upper and lower bars or "whiskers" denote the data's maximum and minimum, respectively. Box plots of the observed whole-body concentrations of fish in the middle Animas River provided by the Southern Ute Indian Tribe (SUIT 2015) and the U.S. Bureau of Reclamation (USBR 1996) are also shown in these figures. There was reasonably good agreement between simulated and observed concentrations, especially at Durango where the ambient water concentrations are similar to those on the SUIT reservation.

With the exception of lead, these plots show that whole-body metal concentrations declined from Silverton (RK 64) to Durango (RK 94 in this study) and from Durango into SUIT reservation (RK 100 to 132). Whereas copper declines are very modest, the declines in cadmium and zinc concentrations were very pronounced and could be readily attributed to the differences in ambient concentrations of these metals in the upper and middle Animas River. Although lead concentrations in Silverton fish were lower than those at Durango, lead concentrations in Durango fish appear to be distinctly higher than those in fish from the SUIT reservation reaches.

Figure 7-2. Box plots of annual background whole-body cadmium concentrations (ug/g wet wt)

Published metal BAFs are highly variable and generally inversely dependent on the environmental water concentrations used to calculate them (Chapman et al. 1996, McGeer et al. 2003, DeForest et al. 2007). During much of the year when water concentration varies relatively little, BAFs are relatively constant and could be used to estimate metals concentrations in fish with some confidence. Rapidly varying concentrations, however, make constant BAFs problematic. This is most evident with zinc at Silverton during snowmelt; see Fig. 7-3. At this location, fish are near saturation with respect to zinc. Consequently, as dissolved zinc concentrations decrease during snowmelt calculated fish BAF's must increase resulting in the classic inverse relationship between exposure and body concentrations. It is also important to note that "constant" zinc BAFs from December 31 to April 1 at Silverton and Durango also demonstrate this classic inverse relationship between exposure and body concentrations. In particular, although Durango has much lower dissolved zinc concentrations than does Silverton, its fish have much higher calculated BAFs.

Figure 7-3. Simulated dynamics of zinc BAFs

Animas River fishes respond rapidly to metals in their environment. The half -life of metals in these fish vary between 3 and 16 days depending on metal and location (Table 7-10). The half-lives of BASS-simulated whole body concentrations during the average flow year simulations are provided in Table 7-10. Differences between Silverton and Durango partially reflect higher background concentrations at Silverton and significantly lower water temperature which strongly affects bioaccumulation kinetics

Table 7-10. Summary statistics for the BASS-simulated half-lives (days)

Metal Bioaccumulation During the GKM Plumes

BASS was used to model the responses of fish communities to the Gold King plume at Silverton and Durango using the empirically modeled plume water concentrations. The plume varied in length from approximately 14 hours at Silverton to 40 hours at Durango, and dissolved metals concentrations ranged over several orders of magnitude at Silverton and at least 1 order of magnitude at Durango. The BASS simulations of whole body concentrations are displayed in Fig. 7-4.

Figure 7-4. Simulated dynamics of whole-body cadmium concentrations (ug/g wet wt) in 2-3 year old brown trout during the GKM plumes at Silverton and Durango

BASS predicted that despite the relatively rapid passage of the GKM plumes, the fish likely responded by accumulating metals quickly. The notable exception to this forecast was zinc bioaccumulation at Silverton, where only a very small response to the large concentrations of metals was predicted. Here, fish are already near saturation levels for zinc from chronic exposures. Consequently, they would unlikely to respond significantly to the additional zinc loadings represented by the Gold King plume. Zinc stays within the aqueous phase within the fish and is very mobile so the fish gives it up easily.

Elevated levels were short-lived as the fish also depurated the metals quickly. It generally required about 4 half-lives to completely eliminate the metals accumulated as the GKM plume passed. Most metals were eliminated in about 8 to 12 days after the passage of the plume at Silverton (August 13) and Durango (August 19) respectively.

As predicted for the background BAFs of metals during snowmelt, metal BAFs calculated for fish during the GKM plumes and Silverton and Durango are inversely related to their instantaneous dissolved water concentrations. Table 7-11 summarizes the regression equations that can be used to characterize and to calculate BAFs during the passage of these plumes.

Table 7-11. Summary of the regressions characterizing the relationship of BAFS

Ecological Impacts due to Metal Bioaccumulation

One way to evaluate the potential effects of the GMK plumes of exposed fishes is to compare their accumulated whole-body concentrations to observed whole-body concentration that are known to have caused either no observable ecological effects or quantifiable ecological impacts. The use of such comparisons is based on the simple assumption that chemical concentrations which are internal to an organism are inherently more accurate for assessing onset of toxic responses in organisms than are external environmental concentrations or benchmarks (e.g., LC_{50}).

Table 7-3 summarizes whole-body residue-based NOELs (No Observed Effects Levels) for growth, mortality, and reproduction effects on juvenile and adult fish that EPA complied for this assessment. Table 7-4 summarizes compiled whole-body residue-based OELs (Observed Effects Levels) for growth, mortality, and reproduction effects on juvenile and adult fish.

Background whole-body concentrations of all metals in 2-3 year old brown trout at both Silverton and Durango were completely within the range NOELs reported in Table 7-12. In terms of OELs, however, background concentrations of cadmium and zinc in these trout were greater than the minimum OELs [i.e., Lowest Observed Effects Levels (LOELs)] reported in Table 7-13 at both locations. Whereas Silverton trout lead concentrations were higher than the lead LOEL, Durango trout lead concentrations were lower than this benchmark. See Figures 7-1 through 7-4.

Table 7-12. Summary statistics for published whole-body residue-based NOELs

Table 7-13. Summary statistics for published whole-body residue-based OELs

During the GKM plume at Durango, whole-body concentrations of all metals in 2-3 year old brown trout were within the range NOELs reported in Table 7-12. During the Silverton plume, however, only cadmium and zinc concentrations in exposed trout were within this range of NOELs. In terms of LOELs, whole-body metal concentrations of Silverton and Durango trout exceeded all assumed LOELs with the exception of copper concentrations at Durango. See Figures 7-1 through 7-4.

Because there is a wide range of NOELs and OELs reported for the metals in Tables 7-12 and 7-13 which overlap significantly, there is no one critical body residue (CBR) or CBR-like threshold for each metal and fish species. Rather, depending on the endpoint of concern (i.e., survival, growth, reproduction, etc.), there is a range of CBRs which are useful in making objective and well defined ecological risk assessments. These CBRs, however, will vary not only by the species of concern but also by that species life history (i.e., age, body weight, trophic position etc.) and exposure history. Although this approach has uncertainties and variability, it can be combined with other information (e.g., water quality thresholds etc.) to make objective assessments and decisions.

Although major ecological impacts on Gold King plume-exposed fish would not expected at either Silverton or Durango based on the preceding NOEL comparisons of BASS-predicted whole-body metal concentrations, it is also clear that these fishes are probably ecologically compromised chronically based on known ranges of OELs based on bioaccumulation modeling. This analysis only analyzed published whole-body NOELs and OELs for the growth, mortality, and reproduction of juvenile and adult fish. Impacts on egg and larval hatching and survival were not considered. Nevertheless, this assessment is consistent with that of Besser and Leib (2007) who concluded that fish populations in the upper Animas at Silverton are impaired by chronic acid mine drainage, especially as related to zinc and copper.

Studies of fish and benthic communities have been conducted in the Animas River following the Gold King plume. The Mountain Studies Institute recently released a report on studies of benthic macroinvertebrates (BMI) communities in the upper Animas River following the Gold King release through the Fall 2015 (MSI 2016). This study found benthic macroinvertebrate populations in the Animas River from Silverton to Durango appear to have largely survived exposure to high metal concentration associated with the Gold King Mine release. Additionally, Colorado Parks and Wildlife data indicate that fish populations in the Animas River were not impacted by the Gold King Mine release (White 2016). All species present before the plume were present after the plume, and there were no differences in BMI community health metrics from 2014 to 2015. They note however, that copper tissue concentrations were higher in 2015 than in 2014 at all sites affected by the Gold King Mine release. This results was consistent with this bioaccumulation analysis.

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CHAPTER 8: WATER AND SEDIMENT QUALITY POST GKM EVENT

Metals concentrations were elevated during passage of the Gold King plume throughout the Animas and San Juan Rivers (Chapter 4), and receded back towards pre-event conditions within days after plume passage. For example, the summed metal concentration in the Animas River at Durango during the plume and for several weeks afterward is shown in Fig 8-1. Typically, dissolved major cations (calcium, magnesium, potassium and sodium) are the dominant constituents in water during August while concentrations of other metals are quite low. Water quality displayed this pattern within days after plume passage.

Figure 8-1. One month of water quality at Durango.

The Gold King plume left most of the metals released from the mine and entrained between the mine and Cement Creek as deposits within Cement Creek and the Animas River, and to a lesser extent in the San Juan River. The deposits were primarily transported particulates, aggregated colloids (flocculants) and precipitates that likely had a variety of particle characteristics and mineralogies such as gypsum, gibbsite, ferrihydrite and others (See Appendix C).

Several phenomenon could determine how these deposits would continue to influence water and sediments over time. Deposited minerals would have varying chemical and physical stability in the short-term as water returned to background pH and chemical composition. Some could dissolve while those that remained would continue to undergo "aging" towards increased internal crystalline stability. Geochemical reactions associated with deposits could affect water chemistry and sediment metals (Spruill 1987) for a period after initial deposition, thus influencing water chemistry during the low flow fall months where dilution is low. Especially of concern is the physical remobilization of deposits during high flows, such as prolonged spring snowmelt or storms. The rivers experienced spring snowmelt from April through June 2016 and some areas were subject to large fall storms.

This chapter examines trends in water and sediment metal concentrations, with a focus on determining detectable impacts on post-event water and bed sediment metal concentrations as a result of material deposited in the river system. A longer term monitoring program has been established to study trends over the next several years and monitoring results will be reported in greater detail elsewhere. This chapter briefly probes where, how long, and to what level were metal concentrations changed in the Animas and San Juan Rivers immediately after the Gold King release and within the 10 months following the Gold King release and wht those post event patterns implied about the fate of the Gold King metals.

The primary questions addressed following the Gold King release and passage of the metals contaminated plume through the Animas and San Juan Rivers are:

- Even though metals concentrations in the water and streambed declined towards background levels, did they reach and then persist at those background levels?
- Did plume deposits impact post event water quality relative to pre-event conditions?
- Will there be a second wave of contamination in later high flows from the re-suspension of deposited material?

Overall Patterns in Metals Concentrations

There is significant spatial and temporal variability in water conditions and metal concentrations in the large geographic area contributing to the Animas and San Juan Rivers due to natural differences in geology and climate and historic impacts of land use and mining. Analysis of Gold King plume movement through 600 km of the combined rivers in earlier chapters identified some of this pre-existing spatial and temporal variability in water column and sediment metal concentrations. The Gold King plume added a veneer of metals to existing deposits that exhibit pre-existing patterns. The challenge for post-event analysis is to determine the longevity of the deposited material and subsequent fate within the natural temporal variability of processes that control the water chemistry of these diverse rivers.

The longitudinal patterns of metals concentrations in water and sediment are shown in Figures 8-2 and 8-3, respectively. These figures concisely present more than 1400 water and 700 sediment samples collected during and after the Gold King release. Longitudinal patterns follow pre-existing patterns shown by the USGS basin-wide AMD studies. Studies identified water quality impacts arising from natural geologic processes and historic mining in the Animas River headwaters and offsite ore processing (Church *et al.* 2007, Church *et al.* 1997). Longitudinal patterns were strongly evident in the Gold King plume (Chapter 4), in surface water quality (Chapter 7) and in historic data for bed sediment metals (Chapter 6). There is a steep longitudinal gradient along the Animas River emanating from the ore-rich and AMD contaminated headwaters.

Figure 8-2. Longitudinal trend in water

Figure 8-3. Longitudinal trends in beds.

Concentrations also vary temporally at individual locations as captured by repeated sampling. Some of this variability reflects natural processes. Most importantly, streamflow is an important driver of metals concentrations in the water and perhaps in the streambed (Church et al. 1997; Spruill 1987).

Sediment concentrations of many metals including lead were historically high in the upper Animas river Fig. 6-18). Plume deposits were especially high in lead in the upper Animas as evidenced by samples collected at multiple locations within this reach after plume passage (Fig. 8-4). Temporal variability of metal concentrations was also high in the month after the Gold King release as illustrated by lead sediment samples (Fig. 8-4). Data points are colored reflecting time since the plume passed (red immediately after, moving to cooler colors over time). Over the next several weeks after the plume, lead in some of those locations had already begun to decline towards the segment average but sampling also reflects the spatial variability of deposits.

Figure 8-4. Lead in sediments longitudinal

Site-specific variability evident in metals concentrations in Figures 8-2 and 8-3 is at least partially determined by streamflow in each location. The importance of streamflow in determining concentrations of metals in water was introduced in Chapter 6 where it was shown that metal concentrations correlate either positively or negatively to streamflow, depending on whether dissolved or particulate/total. The general patterns of streamflow in various locations in the large geographic area are important for interpreting patterns of metals concentrations over time in those locations. This is especially the case for analyzing potential mobilization of Gold King deposits, a main concern for post-release water quality.

The hydrographs at an upper Animas River location between Silverton and Bakers Bridge and at a lower Animas River gage in Farmington from the time of the Gold King release through spring snowmelt 2016 are shown in Fig. 8-5. Although there were several freshets in the upper Animas, flow generally declined during the 10-month period and the flow observed during the Gold King plume was not seen again until mid-April on the rising limb of snowmelt. The lower Animas and San Juan Rivers experienced at least 3 comparable flows within the months after plume. Thus, trends in metals and processes that control them likely varied spatially within different segments of the Animas and San Juan Rivers in the post-plume period.

Figure 8-5. Animas hydrographs.

The relationship of metal concentrations to flow was evident in the post-event fall 2015 and snowmelt 2016 sampling. In the weeks following the release, receding streamflow increased concentrations of dissolved metals, illustrated by zinc at Silverton in Fig. 8-5C. Fig. 8-5D shows examples of elevated aluminum concentrations that coincided with three high flow events evident in the hydrograph. The relationship between metals and streamflow influenced patterns of metal concentrations and was important to control for in statistical analyses and interpreting temporal patterns of metals in water.

Analysis of Temporal Trends in Metals Concentrations

This analysis focuses on temporal trends in metal concentrations in water and sediment throughout the Animas and San Juan Rivers after the passage of the Gold King release using water and sediment data collected primarily since the Gold King release.

The analysis moves downstream beginning with the headwaters and emphasizes the most important and dominant trends following Gold King in each area in broadly defined segments of the rivers that had reasonably uniform behavior and response to the Gold King release. There are far too much data to exhaustively assess each location in this report. The intent is to connect the post-event response of water and sediment to the initial plume effects in the critical period of time immediately following the event. Observational data are presented graphically for the 10 months following the event, including the spring snowmelt in June 2016, concentrating in each geographic area on the most salient observations and probing potential cause and effects. Potential differences in metals concentrations prior to and following the Gold King event were statistically tested at the few locations where sufficient historic data were available.

Discussion varies geographically depending on availability of data and the nature of trends that become evident. Analysis is grouped for sampling locations in the Animas River: Upper Animas includes the segment from RK 12.5 to RK 16.4 that includes sampling sites in Cement Cr and Animas below Silverton. The Middle Animas extends from RK 16.4 to RK 132 and includes major sampling locations at Bakers Bridge (RK 64.0), and multiple sites in Durango and in the Southern Ute Indian Tribe Reservation. The Lower Animas includes the river segment from RK 132 to the confluence with the San Juan at RK 191 in Farmington New Mexico. The San Juan river is also grouped into the Upper San Juan from RK 191 to RK 214 that includes Farmington to Fruitland. The Middle San Juan includes the segment from RK 214 to RK 296 with major sampling locations in the area of Ship Rock and Four Corners. The Lower San Juan includes the river segment from RK296 to RK 550 at Lake Powell that includes major sampling locations at Montezuma Creek, Bluff UT and Mexican Hat UT.

Post Gold King Release Data Sources

Water and sediment monitoring has continued in the year following the release to understand the long term impacts of the release and post-event adjustments and processing of deposited material. Almost 1,400 water quality samples have been collected from the Animas and San Juan Rivers both during and following the Gold King release. Samples were collected by EPA, states, tribes, municipalities and NGOs. The data sources described in Chapter 2 and Appendix A provided data used in these analyses. Most of the post-event samples were collected in August through October 2015. Since the fall, data providers have scaled back frequency of sampling and applied a longer term monitoring strategy at key locations and less frequent sampling. Monitoring during 2016 snowmelt was a major emphasis with sampling intensifying from April through June 2016. As with plume analysis, observed data were compiled from multiple sources and presented collectively with all the inherent variability associated with differences in methods.

Availability of post-event data allowed evaluation of trends after the release. Establishing whether water quality returned to pre-event levels required comparison to samples collected prior to the release. Various studies, monitoring programs, and routine sampling at USGS gages have generated historic data for metals concentrations in water and sediment in the Animas and San Juan Rivers prior to the Gold King release. Pre-event data were distributed longitudinally along the Animas and San Juan Rivers allowing some comparisons throughout the Gold King affected. However, pre-to-post comparisons were dependent on the availability of data, which were limited to a few locations with inconsistent coverage of water and/or sediment, total versus dissolved fractioning of water samples, or coverage of specific metals. Sources of historic data are listed in Table 8-1.

There was greater uncertainty associated with differences in sampling and testing methods within the historic data than in the post-event data, although important laboratory and metadata was available. Wherever possible, analysis was restricted to data collected in the last 15-20 years, especially in the upper Animas river segments. Although more historic data exists for some locations, long-term watershed changes could make very old data less reasonable for comparison to post-event samples.

Table 8-1. Historic data sources.

Statistical Methods and Presentation

The importance of addressing the effect of flow on metal concentrations in water and sediment is illustrated for historic and post-event data collected in the Animas at Silverton and Durango in Fig. 8-6. Post-event concentrations followed the same pattern in relation to flow as the pre-event data.

Figure 8-6. Comparison of dissolved for 3 metals pre and post Silverton.

Statistical comparisons of pre- and post- event data included only data within comparable flow ranges to account for the relationship between flow and concentrations. This restriction reduced available data at most sites and eliminated the opportunity for statistical comparison at sites with limited data, such as Baker's Bridge. Statistical comparison of pre- and post-event concentrations of dissolved arsenic and cadmium at Durango in a narrowed range of flow is illustrated in Fig. 8-7.

Figure 8-7. Pre and post comparison of arsenic at Durango

Statistical analysis was performed on aluminum, cadmium, copper, iron, lead, manganese, and zinc. Major cations (calcium, potassium, magnesium and sodium) were not evaluated. The majority of samples for a number of trace metals were near detection limits, and metadata suggested that detection limits varied among datasets. The impact on statistical testing can be large when the majority of samples are reported at the detection level, so statistical comparisons were not performed for these metals. These considerations led us to focus on the seven listed metals. Where non-detects occurred (rare for these seven metals), the concentration was set equal to the detection limit.

All measured concentrations were log-transformed. Two statistical tests were performed for each metal: a parametric t-test assuming unequal variance in the two samples, and a non-parametric

Wilcoxon test. Reported p-values are for two-tailed tests, which are used when either result may be of interest, (e.g. Sample A significantly higher or significantly lower than Sample B)

Some sites were only sampled a single time in the snowmelt 2016 period or in the pre-event period, which hampered formal statistical testing for pre-event versus post-event differences in water quality. For these instances, Z-scores were used to quantify the magnitude of the deviation of the single observation from a group of observations taken at a specific location and time. The Z-score for the single observation was calculated as:

(SO – GM)/GSD

where SO is the single observation measurement, GM is the mean of the group of observations, and GSD is the standard deviation of the group of observations.

For data sampled from any distribution (normality need not apply), Chebyshev's Inequality (Kvanli, Pavur and Keeling, 2006*)* says that at least 89% of sampled values will fall between +/- 3 standard deviations of the mean. Given this result, we considered the single observation to be markedly different from the group of data if the absolute value of its Z-score was => 3.

Statistical results are summarized in tabular format by location in Tables 8-3 to 8-10. Tables provide the pre-event mean concentration, post-event mean concentration, and significance levels (p-values) for both statistical tests. To facilitate visual interpretation, results in the tables are color coded according to the scheme shown in Figure 8-6. Yellow indicates statistically significant increases in post-event concentrations compared to pre-event concentrations. Other colors grade relative to the strength and direction of change of post-event samples.

Figure 8-8. Table color coding.

Upper Animas River Post Event Trends

Cement Creek (RK 12.5). Cement Creek has historically high concentrations of dissolved and total metals, due both to natural geology and mine discharge. Cement Creek experienced the highest concentrations of metals during the Gold King release and also received some sediments eroded from the mine waste pile. Since the release, EPA contractors have constructed a treatment facility at Gladstone near the junction of the North Fork and Cement Creek that receives all of the effluent from Gold King. They have also recovered eroded material from the creek and stabilized the recovered sediment, the waste pile and the interior of the mine (Fig. 8-9).

Figure 8-9 Photos of Cement Creek today.

The facility tracks effluent rate of flow and samples metals on a frequent basis (Fig. 8-10). Flow rate from the mine varies over the year, sharply increasing during the peak of snowmelt. Metal concentrations average somewhat lower than the estimates used in Chapter 3 to determine the mass of material spilled from the mine. The facility received 733,000 kg of Gold King metals from October 2015 through July 2016, and removed 79%. Cement Creek received approximately 150,000 kg of metals from Gold King during this period (Fig 8-10B). Treatment statistics are provided on a monthly basis in Table 8-2. The facility was effective in removing metals during a large spike in inflow during snowmelt (Fig. 8-10B).

Although treatment has removed a large mass of metals from the Gold King mine, there are numerous other mines in the watershed that also impact Cement Creek. Cement Creek continues to have prominent yellowboy coloring as there are multiple mines in the watershed leaking AMD to the stream.

Figure 8-10. Treatment facility efficacy and weekly statistics.

Table 8-2. Treatment facility statistics

The time trace of all samples collected since 8/5/2015 show some trends in metals since the release. Time series of post-event water concentrations (total) of 8 metals in Cement Creek sampled since August 2015 are shown in Fig. 8-11. All metals have declined since the release. Concentrations tended to increase slightly during the late summer months, following expected low-flow patterns (Spruill 1987). Concentrations did not increase during the spring snowmelt as might be expected given that peak flow in 2016 was the fourth highest observed in 20 years of record at the USGS gage (provisional).

Figure 8-11. Time sequence of total metals Cement Cr. .

Despite observed trends toward lower concentrations evident in post-event water concentrations (Fig 8-11), many dissolved and total metals statistically increased in Cement Creek relative to pre-event observations (Table 8-3). (Recent snowmelt data are not included in these comparisons.) The majority of the change was made up of particulates, especially iron, and some additional aluminum and manganese. Increased particulates could reflect treatment effects on water chemistry and/or materials left behind in the stream during the release.

Table 8-3. Cement Creek Statistical comparisons

Bed sediment concentrations are compared in Table 8-3. Note that there was only one pre-event sample, so the previously-described Z-score approach was used to give this sample context relative to post-event samples. The post-event streambed was elevated in lead, copper and cadmium relative to the historic sample, while iron decreased significantly.

Animas River at Silverton (RK 16.4). The Animas River below Silverton is measured at a location known as A72. This site receives AMD contaminated water from the entire upper Animas watershed. Cement Creek makes up approximately 20% of the flow. Post-event water concentrations (total) of 8 metals sampled at A72 since August 2015 are shown in Fig. 8-12. Metals declined after the plume and remained steady or slightly elevated during the low flow fall period. Lead increased somewhat during spring snowmelt while other metals declined.

Figure 8-12. Time trace of water samples at Silverton.

Statistical comparisons of pre- and post-event water and bed concentrations are provided in Table 8.4. Dissolved metals generally increased in the post-event period relative to pre-event for most metals, and were statistically significant for several metals. Total concentrations of iron and copper were also elevated. Sediment metal concentrations decreased or remained the same relative to pre-event conditions. Most notable was a large decline in sediment aluminum and iron, but all metals were lower.

Table 8.4 Animas at Silverton. Statistical comparisons

Metal concentrations in bed sediments from August 2015 through snowmelt in 2016 is shown in Fig. 8-13. Concentrations of aluminum, iron, and trace metals remained relatively constant during the fall period in the Animas below Silverton at RK 16.4 (B and C). During snowmelt (A and B), concentrations of iron and aluminum remained the same while trace metals such as lead and copper increased.

Figure 8-13. Sediments in Animas at 16.4

The Animas River near Silverton is impaired from historic mining and ongoing AMD, and does not have many designated beneficial uses, including supporting aquatic life. Average historic metal concentrations during the fall exceeded many of Colorado's aquatic chronic criteria to support life, although concentrations do not exceed acute criteria on average. The status of the Animas River at Silverton did not change relative to chronic and acute water quality criteria for most metals after the Gold King release, except copper, which increased above the chronic threshold on average (computed at low hardness). Copper has previously been identified as potentially toxic to fish and zinc to benthic communities in this area in earlier USGS (Besser and Leib 2007) and EPA studies.

Middle Animas River Post Event Trends

The middle Animas River includes sampling sites from Bakers Bridge (RK 64) to the Southern Ute Indian Tribe Reservation at approximately RK 132, near the border between Colorado and New Mexico. There are many sampling locations within this segment that were monitored by a variety of agencies and NGO's during and after the Gold King plume. Historic samples were available at several locations. Samples in nearby proximity were combined for graphical presentation but not for statistical comparisons.

The river segment between Bakers Bridge and Durango area was an important depositional zone during passage of the Gold King plume. WASP-estimated depositional patterns are shown in Fig. 8-14.Modeling estimated that between 90,000 to 140,000 kg of metal mass (up to 30% of plume total) settled between Bakers Bridge and Durango (Chapter 6). Another 180,000 likely deposited upstream of Bakers Bridge.

Figure 8-14. Middle Animas Reach and Deposition.

Bakers Bridge (RK 64.0). The time series of consecutive water samples showing total concentration in water of 8 metals in the Animas River in the vicinity of Bakers Bridge sampled from August 2015 through June 2016 is shown in Fig. 8-15. There are no pre-event water samples for statistical comparison at this location. The plume was sampled very near peak and two samples were collected before arrival of the plume as the only representation of pre-event conditions.

Figure 8-15. Bakers Bridge water concentration

After a sharp peak during the plume, water concentrations of most metals declined over the next 2 to 4 weeks. Some reached levels observed prior to the arrival of the plume (Pb, Ar, Mn); others did not reach the lowest levels previously observed during the summer lower flow period (Al, Fe, Cu, Zn). Small increases in zinc, copper, and cadmium during the fall were consistent with expected low flow patterns (e.g. Fig. 8-5).

Lead in both the water and sediment showed the most remarkable patterns at this area. The plume was high in particulate lead. Total water concentrations of lead within this reach exceeded Colorado 1-day domestic supply criteria of 0.05 mg/L for several days during the plume period (Fig. 8-15) and during a portion of the spring snowmelt period. Rapid decline was evident at the long term monitoring site shown in Fig. 8-15. (Arsenic and copper also showed the same pattern as lead at this site.). Baseline concentrations are high but elevated concentrations did not persist in the sediments. Other metals fluctuated through the fall months (e.g. cadmium) or increased following the surface water concentration (e.g. zinc) (Fig. 8-15).

The time sequence of metals in sediment at RK 64.0 are shown for four metals in Fig. 8-16. Sediment metals fluctuated widely in the period immediately after the event and during snowmelt. There were differences among metals and there were no clear patterns during the fall months. Metals in the bed were higher at the time spring sampling began when streamflow was already responding to snowmelt.

Figure 8-16. Bed sediments at Bakers Bridge

Despite deposition in this reach, metals in the sediment were not elevated relative to pre-event conditions as paired t-tests were not statistically significant (Table 8-5). Concentrations of all metals actually decreased following the Gold King release during the fall months relative to a limited number of historic samples. Concentrations and sample variability were high in both pre- and post-event datasets (there were no pre-event water samples for comparison). In Chapter 6 it was shown that the mass deposited in the bed during the Gold King plume was not large relative to the pre-existing sediment mass. This appears to be reflected in the lack of difference between post-event concentrations relative to historic samples.

Table 8-5. Bed sediment statistical comparison at RK 64.0

Water and sediment sampling of 2016 spring runoff began April 30 after snowmelt had already begun to ramp up for several weeks (Fig. 8-5A). Mobilization-level flows greater than those at the time of the plume began on April 15. Metals concentrations in the water (Fig. 8-15) and sediment (Fig. 8-16) responded to higher flow. Water samples showed a relatively small increase in concentrations of the typically particulate metals (Al, Fe, Pb, As.) that rose and fell with flow over the 6 week period. Sediment concentrations were initially high relative to the fall months, and declined steadily during the snowmelt through the rising and falling limb of the hydrograph. This indicates that Gold King deposits, along with other sediments, were mobilized during this period. Sampling ended around June 15 before spring runoff was fully complete. At the end of sampling, mean bed concentrations were closer to historic conditions than in the fall (Table 8-5).

Estimated mobilization of Gold King deposits was discussed in Chapter 6. The WASP water quality model ran resuspension scenarios, estimating that Gold King deposits would remobilize producing small incremental increases in water concentrations relative to the flow volume. Part of the observed increase was due to flow alone, as peaks in the upper Animas watershed were higher in 2016 than in recent years and flow levels were higher than in pre-event samples. After integrating the 2016 samples into the empirical daily concentration models, it was shown that the small increase in concentrations was sufficient to transport the estimated mass deposited in the headwaters. See Chapter 6 for that analysis.

Durango (RK 89 to 98). Water and sediment sampling were intensive during and following the Gold King plume in the reach of the Animas River between RK 89 to 99 that includes the city of Durango. Numerous data providers including CDPHE, EPAR8, and NGO's contributed 113 data points shown in Fig. 8-17 in which all samples collected from RK 89.9 to 97.9 are ordered by time.

The plume front traversed through the reach in approximately 3 hours and was sampled at a number of locations. While the distance between sites was important for characterizing the plume as it passed through the area, although consolidating data provided good definition of its characteristics as it passed through Durango. Consolidating samples for longer term trends was not a problem. Note that half of the samples shown on the Figure were collected from August 5-20. Spring 2016 samples are the most recent. Few samples were collected from November 2015 through March 2016.

Collectively, the samples during the plume defined its maximum concentrations. The plume arrived abruptly on the evening of August 6 with the peak at RK 94.2 (Rotary Park) occurring at Aug 7, 1:15.

After the core passed through in the first few hours, concentrations declined more slowly through August 10. Some of these data were used for the empirical modeling of the plume (Chapters 4 and 5), which closely follows the pattern shown in Fig. 8-17. Several samples taken prior to plume arrival indicated pre-existing conditions. The Mountain Studies Institute (2016) have provided detailed reports of trends in water quality and aquatic life following the Gold King release at this location.

Figure 8-17. Time trace of total water samples Durango.

An interesting aspect of the data presentation in Fig. 8-17 is the opportunity to generally compare data among providers. Data gaps result when a provider did not test for all metals in the TAL panel (e.g. iron). Differences in laboratory detection limits stair step concentrations (e.g. arsenic). Unexplained variability creates a "comb-like" or fuzzy effect (e.g. manganese or zinc), revealing the magnitude of differences among closely-timed or spaced samples due to random or systematic differences of methods among providers. Despite the variability, a coherent picture of water quality emerges. Water quality data are presented in this way at a number of locations in this report as an efficient way to present a considerable amount of data. Potential data issues such as those mentioned are not resolved but merely presented. Readers should examine each figure closely in that there is no set time scale and samples are merely presented in order (x-axis is not fixed) and concentration scales vary among locations (y-axes scales are not uniform).

A notable aspect of total metals at Durango was declining concentrations following the Gold King plume through the fall months until spring snowmelt began in 2016. Copper, zinc, and aluminum increased for a brief period between Aug 12 and Aug 15, then continued the pattern of decline. Concentrations of many metals declined below pre-existing concentrations by October, despite decreasing flow during the period that should have stimulated small increases in some of the metals (lower dilution).

There were historic data for total and dissolved metal concentrations in water available for pre-vs-post event statistical comparisons at several locations in the middle Animas reach, including Durango (Table 8-6) and the Southern Ute Indian Reservation at RK 103 to 132 (Table 8-7). Concentrations of both dissolved and total metals in the Animas River at Durango were either the same or lower in the post-event period relative to pre-event data confirming the apparent trends in the time trace plots. The decline in concentration relative to pre-event observations was most notable for iron and aluminum. Total aluminum and iron decreased by 48 and 30%, respectively. Given the small change in the dissolved fraction, this change must have been in particulate concentrations.

Table 8-6 Animas at Durango Statistical comparisons of dissolved and total water.

Pre-event data was also available for the Animas River as it flows through the SUIT reservation with samples collected from RK 103 to RK 132 km. Water concentrations in this reach followed the same patterns as Durango (Fig. 8-17) so they are shown together. As observed at Durango, metals varied little from historical observations and dissolved or total metal concentrations were not significantly different in the pre- and post-event periods (Table 8-7). Dissolved concentrations of several metals declined (cadmium, copper, lead, manganese) while aluminum and iron did not change.

Table 8-7 Animas at SUIT statistical comparisons

Time series of dissolved metals in water combined from data providers are shown in Fig. 8-18. Dissolved metals at Durango did not generally trend up or down, but showed episodic spikes, some quite large. For example, dissolved lead spiked over two orders of magnitude on multiple occasions during the fall, as did copper and arsenic. Dissolved aluminum increase through much of the first week after the plume passed.

Figure 8-18. Time trace of dissolved metals Durango.

The time series of sediment measurements are shown in Fig. 8-19. There are 57 sediment samples collected from the Animas River in the Durango reach with data more evenly spread through the fall and winter months. Sediment metals did not show declines like water concentration. Seven sediment samples collected by CDPHE on August 13-14 show much higher metal concentrations than the general population. They note that their samples reflect extreme cases and may not be representative of general conditions.

With the exception of these samples, sediment concentrations for each metal reside within a range during the fall months with no pattern of increase or decrease. However, a number of metals increased during spring snowmelt. There were no pre-event bed samples available for statistical comparisons for this segment of the Animas River.

Figure 8-19. Time trace of sediment metals Durango.

Water concentrations of all the metals increased with snowmelt runoff (Fig. 8-20). The USGS sampled metals in snowmelt in 1995 as part of the AMD studies in the headwaters of the Animas River (Church *et al.* 1997). Metals concentrations were elevated during snowmelt sampling and showed hysteresis with the rising and falling limb of the hydrograph. Some of the increased concentrations in 2016 could have resulted from mobilization of Gold King deposits and some could be a regular phenomenon related to increased flow.

Total and dissolved concentrations of aluminum in 2016 and historic samples are shown in relation to streamflow in Fig. 8-20 as an example of patterns that were observed for several metals during the spring. Total and dissolved Al was positively correlated with flow (A and C). In 2016, some of the metals appeared very high relative to earlier data, while others fit within the general population at the higher flows. The 2016 data show strong hysteresis (B), with much larger concentrations on the rising limb than observed historically, but similar concentrations at the peak and on the falling limb. Increased aluminum occurred in both particulate and dissolved fractions.

Figure 8-20. Total aluminum water concentration during snowmelt

Four metals are shown in Fig. 8-21 to emphasize the spring snowmelt response. There was a small increase in the sediment concentrations in many metals that can be observed in the later samples. Metals began the snowmelt season at about the same concentrations as in the fall, rose a small amount tracking the hydrograph, then fell back to the starting concentration after the peak.

Figure 8-21. Sequence of sediment at Bakers Bridge during snowmelt

The timing of higher than expected concentrations at Durango was consistent with observed changes in bed character at Bakers Bridge upstream (Fig. 8-22). Metals behavior in the water and sediments at Bakers Bridge and Durango suggests that Gold King deposits were mobilized from the Baker's Bridge deposition zone in the earlier portion of the snowmelt hydrograph. Deposits mobilized in upstream segments appeared to settle for a time in Durango. Bed concentrations had peaked in Durango within the week of May 19 to May 26 while flow did not peaked until 12 days later, on June 6. By the last sample taken, concentrations had returned to levels at the start of spring sampling.

Figure 8-22. Comparison of Bakers Bridge and Durango bed sediments.

The flow peak was relatively large and would have mobilized sediments and metals, as discussed by Church *et al.* (1997) and as evident in the sediment to flow relationship in Fig. 8-20.

Movement of Gold King deposits during spring snowmelt was discussed at greater length in Chapter 6. Pre-event and 2016 data were used to develop daily concentration/runoff models to estimate daily and annual metals transport. The analysis suggested that sufficient additional metals were carried during the snowmelt period at Durango to account for all of the Gold King deposits in the entire Animas River upstream of Durango. Water concentrations observed at upper and mid-Animas sites collectively support that metals in excess of what would have normally been transported during snowmelt were moved, leaving little indication that they remained in the middle reach of the Animas immediately after snowmelt. Summer and fall sampling will be important to confirm that hypothesis.

Lower Animas River Post Event Trends

For purposes of this study the lower Animas River is the segment within New Mexico beginning at approximately RK 134 to the confluence of the Animas and San Juan Rivers at RK 190.2 (Farmington) (Fig 8-23A). There were a number of locations sampled routinely by EPA or NMED within this segment. WASP identified parts of this segment as depositional zones for Gold King metals (Fig. 8-23). Bed sediment sampling along the Animas River confirmed that aluminum and iron concentrations increase within this stretch (Fig. 8-24), although concentration does not necessarily equate to deposited mass.

Figure 8-23. Map of lower Animas reach and WASP.

Figure 8-24. Deposition along system.

The Gold King plume delivered higher concentrations of colloidal/particulate metals than were found in the river prior to the event, although concentrations were much lower at this point in the river than at Durango and northward. Plume analysis found that metals were deposited in the reach, especially within the portion indicated in Fig. 8-23 (RK 147.5 to 162.9) as generally predicted by WASP.

The post-event sequence of water sample concentrations are demonstrated at three monitoring locations on the lower Animas, including the Animas River at RK 151. 6 (below Cedar Hill), RK 162.9 (near Aztec) and RK 190.2 just above the confluence with the San Juan River at Farmington. The Gold King plume concentration and masses were empirically modeled at RK 162.9 and RK 190.2. Other sites within this segment follow the same temporal patterns as the two shown, with slightly different concentrations reflecting their location. Time series of total concentrations of 6 metals are shown at 3 locations including RK 151.6 below Cedar Hill in Fig. 8-25, RK 162.9 near Aztec in Fig. 8-26 and RK 190.2 in Farmington in Fig. 8-27.

Figure 8-25. Time trace total metals site RK 151.

Figure 8-26. Time trace total metals site RK 162.

Figure 8-27. Time trace total metals site RK 190.

Water and bed concentrations of most metals steadily declined for three weeks after the plume passed. Total lead, arsenic, copper and zinc were particularly active during this time. Total lead in the water declined by 1 to 3 orders of magnitude during this period, depending on site. Concentrations for several metals including lead initially declined rapidly, plateaued for a period, than declined steeply again through August 26. Total aluminum tended to behave differently than the other metals by not declining during this interval to the same level or at all (e.g. RK 162.9). Part of the increase was in the dissolved fraction that elevated episodically during this period.

The time series of sediment concentrations of three metals are shown at five locations within the segment in Fig. 8-28. There was a wide range of metals concentrations along the lower Animas, with the highest concentrations found between RK 151.6 and RK 162.9 (indicated these sites are likely historically high deposition zones). Sediment concentrations briefly increased for several weeks after the Gold King plume passed at some locations. Sediment concentrations peaked at most sites by August 12 to 16. At the sites with lower concentrations, on the north and southern end of the segment, sediment concentrations began to decline immediately after the passage of the plume.

Figure 8-28. Time trace of sediment lower Animas.

An intense storm occurred the night of August 26-27 with rainfall of 3 inches recorded at Aztec Monument. The storm generated high flow in the lower Animas, but did not affect the middle Animas including Cedar Hill in the northern portion of this segment. The storm hydrograph measured at Farmington can be seen in Fig. 8-5B. The peak was similar to the June 2016 peak during snowmelt. Two additional storms that affected flow in the lower Animas (and San Juan Rivers) occurred on September 6 and September 24. The flows were large enough in each of these events to re-suspend solids deposited during the plume.

Each storm elevated metals significantly with a subsequent decline back towards pre-event levels, as can be clearly seen in the time series plots. For the August 27 rainfall, storm runoff was rapid and not well-sampled, having peaked during the night. Nevertheless, the storm generated large water concentrations measured long after the hydrograph peak (Fig. 8-29) that equaled or exceeded the Gold King plume concentrations. Comparing sites, concentrations increased from north to south.

Importantly, the August 27 storm effectively mobilized plume-deposited metal-rich sediments in the lower Animas (Fig. 8-28). After the storm, bed sediment concentrations remained low through the fall. One exception was arsenic, whose concentration increased slowly through the fall. The source of metals in the subsequent fall storms is not clear since the middle and upper Animas did not contribute flow to these events. It is also interesting that the subsequent storms strongly affected water concentrations but did not strongly affect the streambed, which is likely the case under normal circumstances (i.e., when no plume deposits are present).

Figure 8-29. Metals mass transported during fall storms in the Lower Animas.

Statistical comparison to pre-event sediment data was possible for the Animas at Farmington (Table 8-8). Metals in sediment in the post-event period were the same as pre-event samples. This location had the lowest concentrations and deposition within the segment as evident in Fig. 8-28.

Table 8-8. Statistical tests at Farmington

The storm carried a significantly greater mass of metals through Farmington than the Gold King plume deposited within the lower Animas. Total metals mass calculated from concentrations of the one sample (collected late in the hydrograph) suggest that Gold King deposits could account for only 3% of the mass transported in this one storm (Fig. 8-29). The two additional storms would have transported similar amounts. Sediments concentrations did not appear to change with the later storms, although water concentrations did respond to each storm by rising with the increased stormflow, and then declining over the following several days.

There were little data available for water or sediment concentrations during the spring snowmelt period of 2016 from the lower Animas. Water and sediment sampled on June 8 and 9, 2016 is included as the last observation in the time series. Bed sediment metals increased at all sites in the lower Animas except Cedar Hill. One sample cannot be statistically tested, but the Z-score approach was used to assess if the single sample from the Animas at RK 190.2 was elevated above pre-event levels (Table 8-8). Sediment lead and copper concentrations appeared high relative to pre-event observations.

The lower Animas received metals transported from the upper Animas over the full snowmelt period, although evidence suggests that Upper Animas Gold King deposits were transported relatively early in the 6-week snowmelt runoff. Water concentrations of most metals were somewhat elevated in the lower Animas in the sample collected very near the hydrograph peak, varying by site and metal. More complete sampling at other Animas River locations showed that water concentrations rose and fell throughout the snowmelt hydrograph (e.g. Animas River at RK 130.2 shown in Fig. 8-30).

Bed sediments appeared to follow that pattern as well. Sediment metal concentrations were elevated in the lower Animas, especially lead, copper, and zinc at each of the sampling locations (Figs. 8-29). Did sediment and water concentrations decline in the lower Animas as snowmelt progressed as observed at Durango, or did deposited material remain behind? Samples from August 2016 may answer that question.

Figure 8-30. Sediment lead during hydrograph at RK 130

To assist comparison of the magnitude of changes to sediment and water metal concentrations in the lower Animas, Figure 8-31 shows the peak concentration of lead during or after the plume (in the case of sediment these could be up to 10 days later), immediately following the August 27 storm, and in the snowmelt sample for all 6 locations in the lower Animas where data were available. Metals deposited in the sediments during the Gold King plume were largely moved out during the August 27 storm. Snowmelt brought more metals into the lower Animas, which, at the peak of snowmelt, were at about 50% of what they were immediately after Gold King plume passage.

Figure 8-31. Bar charts comparing concentrations at sites and times.

Water concentrations in the lower Animas during the passage of the plume were low relative to the upper and mid Animas, but were elevated well above background. Metal concentrations declined towards background over a period of weeks and reached low values after the August 27 storm. Water concentrations rose during each fall storm event, and reverted back towards pre-storm levels in the days that followed. Snowmelt brought metals from upstream and elevated total water concentrations, but to a lesser degree than the fall storms.

Historic data were available for statistical comparisons for dissolved metals only (Table 8-8). Dissolved metals in water are not shown because they generally follow the patterns shown for Durango in Fig. 8-18, although with less variation at this downstream location. The statistical comparisons to pre-event data show no significant differences except for dissolved aluminum and iron, which increased significantly in the post-plume period. Dissolved aluminum and iron rose from 10 to 126 and 7 to 78 ug/L, respectively.

The majority of the material transported in and deposited from the Gold King release was colloidal/particulate iron and aluminum. Most of the statistically significant post-event increases in water or sediment concentrations observed in the Animas River, and as will be shown, in the San Juan River, involved dissolved or particulate forms of aluminum and iron. The longitudinal distribution of dissolved iron and aluminum for the Animas and San Juan Rivers is shown in Fig. 8-32, along with trace metals copper and lead. Data is displayed at immediately post event (samples collected from 8/5 to 8/20), and later (mostly in Sep and Oct 2016). There is a significant increase in dissolved activity in the later period in the lower Animas River (approximately RK 150 to 190).

The statistical means from the tables are also plotted longitudinally in show the generally-increasing trends in dissolved Al and Fe concentrations through the river system (Fig. 8-33, A and B). The mean increases were small but persistent.

Figure 8-32. Longitudinal concentrations.

Figure 8-33. Dissolved Al and Fe longitudinal profile.

This may demonstrate chemical transformations in precipitates through the fall months. indicate that passage of the Gold King plume, large quantities of incipient amorphous Fe and Al minerals formed and settled where they adhered/cohered to the river bottom. When minerals precipitate from solution, more soluble mineral phases generally are the first to precipitate for a combination of thermodynamic and kinetic reasons (Steefel and van Cappellen 1990). Over time, the less stable incipient phases recrystallize to more stable phases.

For Fe, a mineral ripening sequence might be: amorphous $Fe(OH)^3$, short-range ordered ferrihydrite, ferrihydrite, and then goethite (goethite might form directly from ferrihydrite or by dissolution and re-precipitation). For Al, the sequence might be: amorphous $Al(OH)^3$, microcrystalline gibbsite, then gibbsite. The solubility diagrams for Al and Fe are shown in Fig. 8-33E and F. Looking at the Al solubility diagram, data from Farmington places Al at the stable gibbsite solubility limit before the event and at the microcrystalline gibbsite solubility limit afterwards. Durango fell in between these regions and did not change through time. Silverton did not plot on the solubility line, either because of an inaccurate representation of the $SO_4^{=}$ concentration at Silverton, or because of the approximation of the geometric means for pH or Al^{3+}. Nevertheless, it also shifted upward (less crystalline stability) from pre-plume to post-plume. The biggest observed change in dissolved Al and Fe was observed in the lower Animas (Fig 8-32).

Post event statistics indicate that there was a longitudinal pattern in the status of Fe and Al that reflects post deposition reactions within the minerals precipitated and deposited in the Animas River (Fig 8-33). If the river bottom is dominated by incipient phases, the water should tend to have higher solution concentrations. This appears to be the case for aluminum based precipitates which appeared to dominate in the lower reaches of the Animas. Alternatively, if the river bottom is dominated by stable ferric oxides, the stable oxides would act as a sink for any elevated metals the water receives from dissolution of the incipient phases. This appears to be the case for the middle and upper Animas. The iron oxides dominated, and increased relatively in the middle and upper Animas relative to pre-existing conditions (Fig 8-33D.) This condition would explain the decrease in metals observed there. Over time there should be a net transfer of metals from incipient phases to stable.

Figure 8-34 Site 162 correlations.

The weather pattern experienced in the lower Animas and not the middle and upper Animas may have facilitated this change in dissolved metals evident in Fig. 8-32. We illustrate the effect using the correlation of total, dissolved and sediment lead with aluminum as an exemplar for other trace metals such as copper and zinc in Fig. 8-34. The Gold King plume deposited precipitates in the lower Animas at measurably higher concentrations. Aluminum was actually lower than normal during the initial phase, and lead was higher in total and dissolved fraction and very evident in the bed. During the post plume period, concentrations drifted downward towards the expected pattern during the next several weeks. The storm on 8/27 completely reset the system and in subsequent storms lead concentrations were as expected. Lead in the sediment returned to a background conditions as did total and dissolved lead. Lead concentrations increased above expected during the snowmelt the following spring.

The net change in the dissolved and particulate Al and Fe (Post>Pre) concentrations was converted to mass by multiplying by flow over the 3-month fall period (Fig. 8-33, C and D). Since the Gold King event there has been a net decrease in particulate Al in the headwaters, and a net increase in dissolved Al. Particulate iron generally increased in the headwaters. A net increase in dissolved mass of both Al and Fe amounted to approximately 10,000 and 5,000 kg in the lower Animas, respectively. The additional dissolved Al and Fe introduced to the San Juan River moved through without change.

San Juan River Post Event Trends

The Animas River joins the San Juan River at Farmington, NM. From there the plume flowed through approximately 225 km of the river in the states of New Mexico and Utah and the reservations of the Navajo Nation that runs the length of the San Juan and the Ute Mountain Ute tribe) before entering Lake Powell (Fig. 8-35) A mass estimated between 43,000 and 58,000 kg of mostly particulate iron and aluminum along with lead, copper, zinc, and others was delivered over a several day period, but most arrived on August 9, 2015 (Chapter 6). By the time the Gold King plume joined the San Juan, metals concentrations were relatively low due to dilution and deposition of mass distributed along almost 200 km of the Animas River upstream.

On the day the Gold King plume entered the San Juan, flow was approximately equal between the two due a release of water from the Navajo Dam to mitigate impacts of the plume. The San Juan River diluted the plume that arrived by an additional 50%. The Animas River is unregulated, and typically carries a higher percentage of the flow where they merge. Because of the dam release, Sediment and water was much higher than normal on an August day. The Animas carrying the plume joined the San Juan River that was equivalent in flow and concentrations of many metals due to the natural load associated with sediment (Chapter 5). Modeling of plume movement suggested that relatively little of the plume mass likely deposited within the San Juan River. Most deposition would likely occur within the first several kilometers downstream of the confluence of the two rivers and at a few discrete locations along the river primarily where major tributaries join (Fig. 8-35).

Figure 8-35. Location map of the San Juan River and WASP deposition.

Water and sediment has been monitored along most of the length of the San Juan during and since the Gold King release. Most of the measurement is at 8 general locations conducted by various agencies and tribes depending on location. Sampling has been most intensive at 5 of the locations which will be the focus of discussion. Sufficient historic sampling of metals has occurred to allow some statistical comparison of pre- and post-event metals concentrations. The San Juan River is discussed in three segments; the upper San Juan (between Farmington at 196 km and Ship Rock at 246 km), the middle San Juan to Montezuma Creek (RK 345) and the lower San Juan to the last routinely monitored sampling location at Mexican Hat (RK 421). The river at other locations within these general reaches behave very similarly.

The time sequence of total water concentrations for six metals sampled at three locations, one in each of the river segments, are provided in Figures 8-36 to 8-38. The times sequence of lead, copper, and zinc in bed sediments at 5 locations is provided in Fig. 8-39.

Figure 8-36. Temporal trace of total water concentrations at RK 196

Figure 8-37. Temporal trace of total water concentrations at RK 296

Figure 8-38. Temporal trace of total water concentrations at RK 421

Figure 8-39. Temporal trace of sediment concentrations at 3 San Juan locations.

The Navajo dam released water for some period around the Gold King event creating an unusual hydrograph with higher water, sediments, and metals that lasted for a longer period than typically occurs with storm runoff. This broadened hydrograph was seen through the length of the river. The 3 large storm events on August 27, September 6 and September 24 also affected the entire length of the San Juan. Because of the dam release, the plume event in the San Juan River was also equivalent to a storm event in the system.

Metals in the upper San Juan River at RK 196.1 (Fig 8-36) closely followed the temporal pattern of metals in the Animas River at RK 190.2 (Fig. 8-27). (See Fig. 8-27 for the Animas River at RK 190.2). This should be expected given that the Animas usually contributes at least 50% and usually more of the flow to the San Juan. The dam released water for some period after the plume passed creating an unusual hydrography that had water, sediment, and metals elevated for a longer period than typically occurs with storm runoff. The water release affected the entire length of river. The San Juan also responded to the large storm events on 8/27, 9/6 and 9/24. Because of the dam release, the Gold King plume event was equivalent to a storm event in the San Juan River.

At RK 196.6, concentrations of most metals in the San Juan were low but possibly elevated during the time the plume passed due to the river's high flow. Interpreting the association with the plume is not as straightforward as in that the San Juan was also carrying high loads of sediment and metals. Metals in the San Juan tracked the Animas at RK 190.2 but were diluted in proportion to flow. Nevertheless, lead, zinc and copper were particularly pronounced. These metals declined in the days following while aluminum increased, probably related to sediment. Metals increased more significantly in each of the three fall storm events, peaking sharply and receding back towards what appear to be base levels in between.

Total metals concentrations in the middle and lower San Juan were also strongly driven by elevated flow. The middle and lower reaches of the San Juan represented at RK 296.8 (Fig. 8-37) and RK 421.4 (Fig. 8-38) were similar to each other and differ from the upper reaches that are closer to the Animas confluence. Metals respond to the same storm events but with more subdued peaks and prolonged receding limb. The Gold King plume was not readily apparent in the general backdrop of the dam release flow event associated with it at either downstream site.

Metals concentrations in sediment are low in the San Juan River (Fig 8-39), especially when compared to the Animas River Metals are fairly uniform throughout the river, although concentrations trend upward from RK 246.3 to RK 345.8 then decrease to RK 421.5. Sediment concentrations had only a small response to passing storms. During the plume, lead in sediments appeared to be somewhat elevated immediately after the plume passed RK 246.3 and possibly at RK 295.8.

The spring hydrograph was measured once in the upper San Juan and numerous times during the snow melt period in the middle and lower San Juan, so the time sequence at each of the locations has at least one snowmelt sample. Where data is more complete it is evident that metals in the water and to varying degrees in the sediment increased during the spring runoff, including lead, copper, and zinc (Fig. 8-40).

To facilitate comparison of the temporal traces, the total concentration of lead in water and sediments at three important response times are shown in Figure. 8-40 as an exemplar for other metals, although the lead signature was stronger during the plume than other metals (Chapter 5). Six sites along the San Juan are shown and the incoming concentrations from the Animas are include. To represent the plume, the highest measurement during passage of the plume at each location was selected. The individual storms were not evenly measured at each location. Therefore, the largest concentration observed in any of the 3 storms was selected to represent storms.

Figure 8-40. Water and bed sediments at 3 times.

Snowmelt was represented by the highest measurement during the 2016 spring snowmelt season. Water was measured frequently during the spring in the middle and lower San Juan, but just once in the upper San Juan and Animas. Sediment was measured once or twice during the period throughout. Lead (and other metals) clearly elevated. The temporal traces at RK 295 (Four Corners) and RK 421 (Mexican Hat) in Figs. 8-37 and 8-38 have weekly measurements over a the period from February 17 to June 25 that captured the full snowmelt period.

During storms and during the plume, total lead concentrations in the San Juan were relatively high and within comparable ranges. This can also be seen in the temporal traces. Concentrations during the plume were probably also influenced by the dam flow event. Concentrations declined during this “event” through the San Juan River. Storm concentrations represented in the fall 2015 data tended to increase in the downstream direction. This could vary in individual storms based on their direction. At times, such as snowmelt and the plume and dam releases, the flows are driven from east to west. The September 24 storm was a regional event that moved into the watershed from the southwest.

Metals concentration in water clearly rose and fell during the 2016 snowmelt period. Peak concentrations for lead shown in Fig. 8-40 show those peaks were small relative to storms. There was no apparent trend in the downstream direction during snowmelt.

Sediment concentrations during these three periods is shown in Fig. 8-40B. Lead in sediment tracked the same downstream pattern as water during the plume. Lead peaks were much smaller during storms and trended upward in the downstream direction like the water. Lead during 2016 snowmelt was higher than measured during the plume, and was greatest in the upper San Juan but was apparent through most of the river system to at least RK 345. Lead in sediment at RK 421 does not appear to react to react to much. This suggests that Gold King metals mobilized in the Animas could be seen in the water and sediments of the San Juan. The effect on sediments appeared to be greater during snowmelt than during the plume.

Due to the low concentrations of trace metals in the San Juan, a correlation technique was used in plume analysis to detect Gold King metals within the background influence of sediments in transport at the time (Chapter 5). Trace metals were correlated with aluminum or iron as representative of the sediment concentrations. The method was effective in identifying elevated trace metals relative to what should be expected at the level of sediment present in the water. This technique is applied to lead, copper, and arsenic total water concentrations during the snowmelt samples at an upper, middle, and lower sampling location in Fig. 8-41.

Figure 8-41. Water concentration correlation with aluminum during snowmelt.

Total lead, copper, and arsenic concentrations in water were well within the range typically observed in the three locations. However, the all three areas appear to have elevated lead during the spring snowmelt, suggesting the Animas as a source. Copper and arsenic did not appear to be different from typical background concentrations at those levels of aluminum.

The same technique is applied to bed sediment in Fig. 8-42. In this case data include pre-event samples, post Gold King plume samples and those collected during fall 2015, and snowmelt samples grouping all upper San Juan sites (A). Lead is correlated with iron because many samples did not have aluminum data. Some measurements of lead during the plume were elevated but for the most part they are within the typical range. Lead in sediment was elevated in most of the samples collected during 2016 snowmelt when compared to the typical relationship with iron. However Lead concentrations in 2016 snowmelt are plotted longitudinally in (B). There appeared to be more deposition within the upper San Juan, especially within the first 10 km downstream from the Animas.

Figure 8-42. Bed sediment samples snow melt.

There were sufficient data in the upper San Juan for statistical comparison of pre- and post-event sediment metal concentrations. Table 8-9 provides statistical testing results. Pre-event data for lead is shown in Fig. 8-42. Only iron was significantly higher in the post-event period. This is consistent with Fig. 8-42 where iron concentrations were higher during the plume and during snowmelt than any other time. This may reflect the predominance of iron in the Gold King mass. Other metals, including lead, were not statistically different post plume. However, all metals were elevated in the upper San Juan during spring snowmelt compared to pre-event data.

Table 8-9. Sediment concentration statistical tables.

Dissolved Metals San Juan. Time series of dissolved metals are not shown because they are generally fairly uniform through time and very similar from site to site. Baseline concentrations for most trace metals are typically less than 1 ug/L. Background dissolved concentrations were generally similar throughout the San Juan River and varied much less along the length of the San Juan River than observed in the Animas. However, dissolved metals are responsive to the storm events when most metals spike briefly. Aluminum and iron were higher in the lower San Juan than upstream reaches and was very response to storms.

Table 8-10. San Juan River Dissolved metals statistical comparisons.

There were sufficient pre-event data for dissolved metals to statistically compare with post Gold King samples. (Only dissolved metal concentrations were available from historical datasets in the San Juan River.) Table 8-10 provides statistical results. Dissolved aluminum and iron increased significantly after passage of the Gold King plume in all three of the segments of the San Juan River compared to historic data. Relative increases were largest as dissolved aluminum increased from 5 to 10 times and iron increased from 3 to 4 times. Concentrations were low, however, and absolute increases were small. The net increase in aluminum and iron was observed throughout the lower Animas River following the Gold King release as shown in Fig. 8-33. It appears from the mass estimates that the dissolved aluminum input to the San Juan River from the Animas continues to flow through the Animas without change or deposition.

Average metal concentrations in Table 8-9 were historically low relative to the appropriate state chronic and acute aquatic criteria, although average cadmium concentrations were close to exceeding when hardness is 200. The average increase in aluminum and iron did not change this status although mean dissolved Al is now closer to UDEQ warm water fish -4-day criteria. Water concentrations were also compared to water quality criteria adopted by the Navajo Nation from the full reach of the San Juan and the Ute Mountain Ute tribe for the mid San Juan. Results were consistent for all 3 reaches and both sets of criteria.

Effects of the Gold King Plume on Irrigation Ditches

For bed sediment samples collected in the post-plume period in the fall of 2015, we compared samples taken in irrigation ditches from RK 135 to RK 190, where many of these ditches reside, to samples collected in the main river over this stretch of river. Our objective was to identify any major differences between metal concentrations in the two sets of samples, as these differences may be important for the potential use of the ditch water (irrigation of crops and livestock). We used a jittered scatterplot (Figure 8-43) to depict the concentrations of 8 metals in both ditch and main river sediment samples. We draw a distinction between main river samples collected in the immediate post-plume period (up until August 27^{th}) and samples taken after the large rainfall event of August 27^{th}.

Figure 8-43. Jitter plot of irrigation versus mainstem sediment samples.

Although some river and ditch samples in the immediate post-plume period show an elevation in sediment metal concentrations, we see no discernible differences between metal concentrations in irrigation ditches and mainstem Animas River samples.

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CHAPTER 9: POTENTIAL GROUNDWATER EFFECTS

This chapter explores the potential impact of the Gold King plume on floodplain water supply wells. The movement of the plume through the Animas River plume was dramatic and visual; in contrast, the movement of a potential subsurface plume of dissolved components into the alluvial aquifer would be by nature hidden and by mode hypothesized. Nevertheless, there were empirical observations and theoretical models that inform the evaluation of potential for impact. There were hundreds of water supply wells located in the floodplain of the Animas River of Colorado and New Mexico at the time of the release, some located within meters of the river, others kilometers away. Many wells areprivate domestic wells that are primarly low volume pumpers and some were larger volume community wells. It is a relevant question to ask whether there was and is potential for impact In this chapter we explore the potential for dissolved river plume water to have movedout of the river into the alluvial deposits potentially contaminating the transported to the pumping wells

Due to the higher metals concentrations during plume movement, the analysis centers on floodplain aquifers adjacent to the Animas River. It was assumed that most of the time the Animas River continuously gains water from the surrounding groundwater aquifer as it flows from Silverton, Colorado to Farmington, New Mexico, RK 16.4 to 191. When the flux of water is from the surrounding terrain into the river, dissolved contaminants present in the river flow would travel downstream within the river without any input to to the floodplain alluvium, thus providing no exposure pathway to the floodplain water supply wells. If there are locations where the river inputs water to the alluvium (termed a losing reach) then there would be potential for well contamination during and following the event from elevated metals in the water or sediments. High volume pumping can also reverse the natural direction of flow and draw water from the river into the alluvium. A primary objective of this analysis was to identify the extent and characteristics of wells due to their geographic setting or pumping history that may have had the potential for drawing Gold King metals from river water in sufficient quantities to pose a hazard.

EPA and states sampled community and private well water during the Gold King response to address this concern. Groundwater movement requires time to travel through the substrate and one challenge to sampling groundwater was to know when to sample to catch a transient event. Sampling identified one community pumping well within the middle Animas segment located close to the river that had characteristics of a short term increase in dissolved zinc when well raw water concentrations were compared to river concentrations at various dates (Fig. 9-1). Although levels were well below human health advisory levels, an observed spike in well water suggests the potential for exchange.

Figure 9-1. Empirical data of dissolved zinc concentrations at a mid-Animas River community well (RK 66).

Groundwater modeling was used to investigate the potential for water movement from river to wells at the scale of alluvial valleys containing multiple wells. The main chapter emphasizes an overview of groundwater movement and modeling results. Modeling details on data and methods are provided in

River communication with wells: conceptual

The Animas River alluvial aquifer is within the floodplain deposits that snakes between the surrounding terraces and mountains as it winds down from the headwaters at Silverton CO to its confluence with the San Juan River in Farmington NM. See Figure 9-2. There are many water supply wells that tap into the aquifer, including large numbers of private households or domestic wells, community wells, and irrigation wells. Another important hydrologic feature is the use of irrigation ditches to divert the river water to satisfy agricultural fields throughout the floodplain. The local elevation of the river water in comparison to the local water table in the floodplain aquifer determines whether a reach is "gaining" groundwater or "losing" groundwater, assuming the sand and gravel streambed is permeable.

Insert Figure 9-2. The shallow alluvial floodplain aquifer of the Animas River, with emphasis between Aztec and Farmington, NM (RK 170-180).

There is not much known about the alluvial aquifer in terms of spatial heterogeneity and depth.

It is aquifer heterogeneity that offers the potential for preferential pathways, or barriers for that matter, from the river to well. The US Geological Survey (USGS) conducted a detailed study in the upper Animas River watershed near Eureka, Colorado, and a trench study revealed some of the complexity of the stratigraphy and gravel deposits (Vincent, Elliott, 2007). The deposits include high permeable sands and gravels and low permeable silts. See Figure 9-3.

Insert Figure 9-1. Animas River in floodplain near Eureka above Silverton, Colorado.

The actual alluvial aquifer base at a specific location is unknown, but a geophysical survey gives some insight. The Animas Water Company invested in a geophysical/gravimetric survey of the floodplain aquifer of the mid Animas River watershed near Hermosa, Colorado, getting estimates of the base of the aquifer in five survey lines (or cross-sections) (Hasbrouk Geophysics, 2003). The permeable deposits are suspected much deeper (600 to 1000 feet) than the current depth of the community wells in this area (about 100 feet). See Figure 9-4.

Insert Figure 9-2. Geophysics modeling of the shallow floodplain aquifer base elevation based on a gravity survey. A computer modeling exercise can demonstrate a hypothetical situation where a pumping well located in the floodplain can source from the river, and if the river water contained dissolved contaminants passing by, induce those solutes to enter the aquifer and eventually reach the well. This situation is demonstrated with the EPA Wellhead Analytic Element Model (WhAEM; https://www.epa.gov/exposure-assessment-models/whaem2000) as shown in Figure 9-5. The area contributing water to the pumping well, or the well capture zone, is delineated by reverse streamline computations from the well. The well receives some of its water from the river, and some from water in aquifer storage. The degree of dilution can be inferred by the number of streamlines the come from the river compared to those that come from the upgradient aquifer. A breakthrough response to dissolved solute can be mapped by releasing forward particles from the river shoreline and recording arrival times at the well in a histogram.

Insert Figure 9-5. Demonstration of a pumping well capture zone and particle tracking breakthrough histogram using the WhAEM groundwater model for a hypothetical scenario.

This hypothetical case was under the situation where the Animas River was a gaining stream, and the nearby pumping well needed to overcome the hydraulic head gradient in order to directly source river water, and with the river transporting a plume of dissolved metals, establishing a potential exposure pathway. This might be representative of a community well located in proximity to the river and continuously pumping relatively large volumes of water (hundreds gallons per minute). Under the conditions where the Animas River is a losing river, the natural hydraulic head gradient would potentially introduce dissolved solutes associated with a river plume into the groundwater aquifer, thus expanding the possible wells at risk to exposure to include nearby wells of lower pumping rates, such as the domestic or household wells. A groundwater modeling investigation was chosen to further the understanding of these potential exposure pathways for two study areas where community and domestic/private wells are present: (1) the mid Animas River; and (2) the lower Animas River, as shown in Figure 9-6, and described in the next sections.

Insert Figure 9-3. The mid Animas and lower Animas River clusters of community and private wells selected for groundwater modeling analyses.

River communication with wells: mid Animas River floodplain

The mid Animas River floodplain has a known population of water supply wells, including a large number of private/domestic wells, and a limited number of community wells. The previously mentioned community well (35m66km) had the interesting empirical signal. See Figure 9-7.

Insert Figure 9-4. The water supply wells located in the shallow floodplain aquifer of the Mid Animas River (RK 65-72).

The long term Animas River discharge reflects the annual cycle of late spring to early summer snowmelt runoff, with subsequent decreases in discharge, interrupted by rain events. This is demonstrated for the upper Animas River near Silverton, Colorado, see Figure 9-8(a). The difference between the sum of the cumulative daily stream flows and the measured daily streamflow is inferred to be made up of contributing diffuse groundwater inflow (Q_{GW}) along the Animas River between the upgradient and downgradient stations. The analysis suggests that for this river section that diffuse groundwater contribution is on the order of 10% of river streamflow. The Animas River around Silverton is understood to be a gaining stream most of the time, with groundwater draining toward the river, with some episodic exceptions during mid-summer, as shown in Figure 9-8(b). It is possible that late spring-early summer snowmelt has the potential to send a pulse of water to partially fill the alluvial aquifer.

Insert Figure 9-5. Streamflow analysis of the upper Animas River near Silverton, Colorado.

The goal of the computational modeling approach undertaken was to capture the essence of the regional groundwater flow system and explore groundwater-surface water interactions under the influence of pumping wells. The step-wise and progressive modeling approach and calibration strategy is described in detail in Appendix D.

The analytic element computer program GFLOW (v.2.2.2) was used to solve for regional and steady groundwater flow in single-layer aquifers (Haitjema 1995). GFLOW is well documented and accepted within the groundwater modeling community (Hunt 2006; Yager and Neville 2002), particularly when applied to shallow groundwater flow systems involving groundwater/surface water interactions (Johnson and Mifflin 2006; Juckem 2009) and for recharge estimation (Dripps et al. 2006). The mathematical foundation of the semi-analytic model includes equations that express the physics of steady advective groundwater flow within a continuum; continuity of flow and Darcy's law (water flows down the hydraulic potential gradient) are satisfied at the mathematical elementary volume.

Sometimes conceptual complexity, particularly at the local scale, suggests numerical modeling techniques. For this project, we used the MODFLOW-NWT and MODPATH (particle tracking) solvers within the Groundwater Modeling System (Aquaveo, GMS v 10.1). The USGS MODFLOW model is the most widely used groundwater flow model in the world. MODFLOW uses the finite difference numerical solution technique, with grid-based rows and columns defining three-dimensional cells, allowing simulations of multi-layer aquifers, non-horizontal base elevations, and opportunities to vary hydraulic conductivity, porosity and storativity cell by cell (Harbaugh 2005). MODFLOW has undergone 30 years of development and quality testing by USGS.

The GFLOW model was used for the initial regional scale and local scale modeling of steady state flow. The regional models provide initial boundary conditions for local scale transient and full 3D modeling using MODFLOW. The progression in conceptual complexity and the utility of the GFLOW and MODFLOW models are mapped in Table 9-1.

Table 9-1. Model synopsis.

The regional GFLOW model construction and calibration for the mid Animas River floodplain wells is described in Appendix D. See Figure 9-9. The model was compared to the static water levels reported at the time each of the wells were drilled. The water balance was calculated for the August 2015-October 2015 period based on USGS gaged water flows at Tall Timber Resort and Durango, Colorado.

Figure 9-6. GFLOW layout of analytic elements for the mid Animas River floodplain groundwater model.

The GFLOW model predicted that only a small number of wells would source from the Animas River, and all of them were located in the upper section between Bakers' Bridge and Hermosa. See Figure 9-10. A possible explanation from geomorphology is that in this region the Animas River flow spills into the floodplain aquifer deposits after traveling through the impervious metamorphic mountain geology. For the full set of wells in the mid Animas River floodplain, over 300, distance from the river was not predictive of sourcing. There were many wells within 125 meters of the river that did not have capture zones reach the river.

Figure 9-10. GFLOW model of the mid Animas River floodplain near Baker's Bridge (RK 65-72) showing groundwater-surface water interactions for the averaging period August-October 2015.

The GFLOW model predicts the community well (35m66km) would source from the Animas River under a variety of conditions. The full sensitivity analysis is presented in Appendix D. The combination of parameters (low recharge, high alluvium hydraulic conductivity, high well pumping rate, low alluvium porosity) that creates the earliest breakthrough of 25 days is shown in Figure 9-11.

Figure 9-11. GFLOW capture zone and breakthrough histogram for mid Animas community well (35m66km).

River communication with wells: lower Animas River floodplain

The lower Animas River of New Mexico also supports a number of community wells and domestic/ household well, along with a highly active system of diversions of river water to irrigation ditches. See Figure 9-12.

Figure 9-7. Community wells (orange) and select private wells (red) for the Lower Animas River floodplain study area.

The New Mexico Bureau of Geology and Mineral Resources (NMBGMR) has embarked on a timely suvey of synoptic water levels in the lower Animas River between Riverside and Farmington and private water levels post the GKM release of August 5, 2015 (Timmons et al., 2016). The water levels provide the potential to have empirical evidence of segments of the Animas River that might be losing water to the aquifer. Their surveys released so far have included observations in August 2015, January 2016, and March 2016. The January 2016 data represents the water table under "baseflow" conditions and not under the influence of mountain snowmelt runoff or irrigation ditches. See Fig. 9-13. There are a number of wells indicating a negative gradient in this section of the lower Animas River between Riverside and Farmington, New Mexico. The negative hydraulic head gradient would suggest that in these sections the Animas River are losing water to the aquifer during the January time period. Most of the potential losing reaches are in the northern half of the study region for this time period. The sporadic spatial distribution of the potential losing reaches underscores the site specific nature of the phenomenon.

Figure 9.13. High resolution synoptic survey of the river water levels and well water levels in the lower Animas River floodplain, January 2016, between Riverside and Farmington, New Mexico.

The NMBRMR also monitored continuous precipitation and Animas River and irrigation ditch stages at select locations. See Figure 9-14. As would be expected, the Animas River stage elevation responds very quickly to precipitation events. The alluvial well in this location has a more muted and delayed response to the precipitation/river stage signal. About a 5 day delay in the signal from river stage to well response is recorded based on observations at an alluvial well. Also, the influence of the irrigation ditches is apparent. Once the irrigation ditch is shut down for the winter, the water levels in the alluvial well drop to the baseflow levels.

Figure 9-8. Hydrographs from Aztec area including a well with continuous data recorder plotted with influences from precipitation and Animas River stage and ditch gage height.

The NMBGMR synoptic water level data was an important constraint on the GFLOW model calibration for the lower Animas River study area as described in Appendix D. The model is used to perform capture zone estimation for the water supply wells, both community and private, and where there was evidence of sourcing from the river, evaluate using particle tracking the breakthrough curves at the well. An average pumping rate for the private domestic water wells was assumed to be 400 gallons per day. The community wells were assumed to pump at the driller's log rated yield. The regional water balance was calculated for the period August-October 2015 based on USGS gaged river flows at Aztec and Farmington. The resulting regional GFLOW model is shown in Figure 9-15. The model suggested that the community well (21m174km) would source from the river under these conditions.

Figure 9-15. GFLOW model of gw-sw interactions in the lower Animas River floodplain

While the GFLOW model predicted the 21m174km community well may source from the Animas River, the first arrival of the plume took over 90 days, and dilution was dominant. The aquifer would take almost 2 years to flush under these conditions (Fig. 9-16).

Figure 9-16. GFLOW capture zone and breakthrough histogram

Empirical Data of Dissolved Metals Concentrations in Wells

Dissolved metals that are most useful as tracers associated with the Gold King mine plume include primarily aluminum and iron, and also manganese, zinc, and cobalt. Together these metals represent about 95% of potentially toxic metals released to the rivers (Utah DEQ, 2015). This section will revisit the hypothesis that dissolved metals in the GKM river plume may have impacted floodplain wells through examination of empirical data (well water quality sampling).

Mid Animas River Floodplain Community Wells

Recall the interesting dissolved zinc signal at a mid Animas River floodplain community well (Figure 9-1). Dissolved background dissolved zinc concentrations in the upper Animas River near Elk Creek are expected to be around 0.08-0.20 mg/l as reported in Church et al (2007, Chapter E9 Quantification of metal loading by tracer injection and synoptic sampling, 1996-2000, Figure 17). The distinction between dissolved phase zinc and colloidal phase zinc in the Animas River is extensively discussed in Church et al. (1997). The observed concentration of dissolved zinc in the plume in Cement Creek was around 30 mg/l.

The observed Animas River surface water quality observations by the Colorado Department of Public Health (CDPH) at the Baker's Bridge area after the passage of the Gold King Mine plume (August 12-18) show evidence that the dissolved zinc concentrations in the river had returned to background levels of 0.09-0.13 mg/l.

The maximum observed dissolved zinc concentrations in the Animas River associated with the GKM plume near Baker's Bridge (RK 65) was about 1.7 mg/l.

The EPA WASP Animas River model gave characteristics of the dissolved zinc plume associated with the Gold King mine release moving past the 35m66km well; the plume would be expected to arrive in the area early in the day of June 6 and take less than 24 hours to pass. The CDPH groundwater quality data at the 35m66km well indicated an elevated dissolved zinc concentration of 0.58 mg/l on August 14, with lower levels observed on August 9 and August 19. Other metals showing an elevated response on August 14 included dissolved copper, lead, and nickel. See Figure 9-17. Metals not indicating an elevated response on August 14 were aluminum, manganese, arsenic, beryllium, cobalt, selenium. pH values were not reported. Iron values were not reported.

Figure 9-17. River and well dissolved and colloidal metals concentrations around RK 66 of the mid Animas River in Colorado.

The CDPHE water quality measurements available in the other mid Animas community wells (75m71km, 650m71km, and 575m71km) did not have noteworthy changes suggesting impact by the acid mine drainage release.

Might the elevated dissolved zinc and other metals be indicative of Gold King Mine plume water entering the 35m66km well? The sensitivity modeling using GFLOW of solute breakthrough times ranged from 25 days to 187 days, based on choice of high or low recharge, hydraulic conductivity of the alluvium, pumping rate of the well, and aquifer porosity. The observed arrival of the dissolved zinc plume at the 35m66km community well was perhaps less than 8 days.

The groundwater modeling analysis did not include complications such as transient pumping and transient river flows, aquifer heterogeneities that might influence dissolve solute dispersion, or reactive transport that would affect metals conversions between dissolved and colloidal forms. The groundwater modeling did not include the potential for clogging of the river bed sediments by algae or precipitated chemicals. The groundwater modeling at the 35m66km well did not include potential pumping interference from nearby private wells, or the influence of irrigation ditches. The modeling did satisfy fundamental continuity of flow and fundamental physical laws of groundwater mechanics, and included the primary process of advective transport of dissolved solute.

In the end, the results of the modeling and empirical evidence cannot rule out the hypothesis that the 35m66km well did pump Animas River water impacted by the Gold King Mine release of August 5, 2015.

The significance of the potential impact is not commented on here. The secondary drinking water standard for zinc, based on taste, is 5 mg/l, and the observed peak well concentration is an order of magnitude below this standard.

Lower Animas River Floodplain Community Wells

There was no clear evidence for water quality impact of the GKM plume on the community wells sampled in the lower Animas River floodplain, between Aztec and Farmington (near RK 163. See Figure 9-18. The dissolved metals concentrations in the lower Animas River associated with the GKM release are much lower than as observed in the mid Animas River, somewhat due to dilution and dispersion, but more likely influenced by geochemistry as segregation into colloidal form occurs. The community wells seem to indicate a fairly consistent groundwater quality concentration for cooper, lead, nickel, and zinc, perhaps indicating the aquifer waters are in a state of equilibrium or long term mixing. The active spreading of river water via irrigation ditches may be a factor.

Figure 9-18. River and well dissolved and colloidal metals concentrations around RK 163 of the lower Animas River in New Mexico.

Summary

There are hundreds of water supply wells in the floodplain aquifers of the Animas River, ranging from continuous larger pumping wells (the community wells) to the small pumpers (the domestic/household wells). There are also intermittent intermediate pumpers (the irrigation wells).

The exposure assessment of the wells to the GKM river plume evaluated the potential for the well to source its water from the river, and if so, the expected breakthrough time of conservative river solutes to reach the well. In addition, dilution of direct river water compared to other sources of water, such as rainfall recharge or deep aquifer contributions, could be estimated.

In the Animas River floodplain, of the hundreds of domestic/household wells investigated, the groundwater modeling suggests only a handful of these wells potentially source from the Animas River and were potentially vulnerable to exposure to the GKM river plume. Given their low pumping rates, the domestic/household wells would most likely need to be located in proximity to a losing reach of the river. The complication is whether any given stretch of the Animas River is either gaining or losing is site specific and temporal. Water balance methods are too coarse to capture the dynamism; a high resolution synoptic survey of water levels during the period of plume passage would be required. The operation of nearby irrigation ditches could play a significant role in elevating water levels in the flood plain aquifers during the growing season, and the elevated aquifer water levels support subsurface drainage toward the river.

For the community wells, because of their higher pumping rates, vulnerability to directly pumping Animas River source water would be mostly controlled by their proximity to the river. The computer modeling suggests that for the community wells investigated (5 in the mid Animas River floodplain of Colorado; 5 in the lower Animas River floodplain of New Mexico), only wells located less than 35 meters from the river received a percentage of water directly from the river with a potential plume river concentration diluted to at least 17%. The modeling suggested the beak-through time of river plume showing up at the well would be at days to weeks.

One community well located within 35m of the mid Animas River floodplain near RK 64 had a chemical signal of some dissolved metals; we could not reject the hypothesis that this signal may have been associated with the GKM plume. But the observed breakthrough time was earlier than suggested by the computer simulations. The raw well water concentrations were below Federal drinking water action levels.

CHAPTER 10: SUMMARY AND SYNTHESIS

On August 5, 2015, an EPA team was investigating the Gold King Mine (GKM) as one of hundreds of mines that is a source of metals contamination in the Animas River in preparation for remediation. Drainage within the mine was dammed behind the collapsed mine structure and rock that blocked the opening of the mine and pressurized the water dammed behind it. While the EPA team was excavating above the main GKM adit, the blockage was destabilized and water began leaking from the mine. The small leak quickly turned into a significant breach that explosively released approximately three million gallons of mine water into the North Fork of Cement Creek that joins the Animas River 13 km (8 miles) downstream. The mine water flooded the North Fork of Cement Creek, and over an eight-day period, the plume from the release flowed down the Animas River to the San Juan River Animas and San Juan Rivers. The mine drained in about 10 hours.

The release traveled as a coherent plume or slug of metals over an 8-day period and through 600 kilometers (370 miles) of the Animas and San Juan Rivers before ultimately reaching Lake Powell. The release crossed three states (Colorado, New Mexico and Utah) and three indian reservations (Southern Ute Indian Tribe, Ute Mountain Ute Tribe and Navajo Nation). EPA worked with state agencies, tribes and local communities through its Unified Command Center in Durango, CO to curb water use and provide alternative supplies during the weeks the release.

USEPA and the states and tribes initiated an extensive monitoring program through the entire river system from the headwaters of the Animas River, through the San Juan River and into Lake Powell. EPA collected samples over varying intervals, beginning at six-hour intervals early in the response and continuing weekly during later phases of the response. EPA, states, and tribes continued to monitor water quality on a less frequent basis throughout the affected river through the Fall of 2015 and through the early spring and snowmelt period in 2016.

ORD scientists have supported EPA's efforts by investigating the transport and fate of metals introduced to the Animas and San Juan River from the Gold King release. The objectives of the research described in this report were to:

- quantify the release from the mine, including what and how much was in it,
- characterize the intensity and duration of potentially high concentrations of heavy metals as the plume moved through the rivers,
- determine the fate of metals within the receiving waters and the streambed,
- assess potential exposures to adverse levels of contaminants in the water and sediments during the plume and in the months following.

Over 1,000 water quality and sediment samples collected by EPA, states, and tribes and others was analyzed and used to quantify the source, transport and fate of the GKM plume (where it went and what happened to it along the way). Water quality, groundwater, geochemical, and bioaccumulation modeling with existing software based process models were employed enabling better understanding of the physical, chemical and biological processes that determined the release characteristics and impact over this large area.

Contamination of the Animas River from past mining has been a concern for decades. Beginning in the 1880s, the Silverton, Colorado area was home to hundreds of mines extracting gold, silver, lead and copper until operations ceased in the early 1990s. Mining and highly mineralized geologic formations created the economically extractable ores in the Upper Animas Watershed has historically discharged an average of 5.4 million gallons of acid drainage per day to the headwaters of the Animas River that contains high concentrations of heavy metals (such as zinc, lead, cadmium, copper and aluminum). The USGS focused considerable research activity in the Upper Animas headwaters from 1995 to 2007 as part of the national research initiative to study and abate acid mine drainage. Information generated in this comprehensive and integrated set of studies was informative to this project.

The release of three million gallons of acid mine drainage was equivalent to four to seven days of current acid mine drainage. The total metal mass in the GKM plume was comparable to a mass of metals carried in one to 2 days of high spring runoff, varying by metal.

How much mine waste was released and what was its composition?

The Gold King Mine released approximately 3 million gallons of low pH (~3) acid mine drainage and 490,000 kg of dissolved and colloidal/particulate metals into the Animas River on August 5, 2015. The mine itself produced a relatively small amount of metals mass (2,800 kg). Most of the mass was entrained between the mine entrance and Cement Creek before reaching the Animas River in Silverton. The majority of the additional mass was eroded from the old mine waste pile that made up most of the hillslope between the mine and the North Fork Cement Creek 100 meters below. The flood could also have entrained or dissolved in Cement Creek where it had previously been deposited.

The Gold King plume delivered very high concentrations of a number of metals to the Animas River where Cement Creek joins it at Silverton over a period of 8 hours. The majority of the released mass was colloidal/particulate aluminum, iron and manganese with significant quantities of lead, copper, arsenic, zinc, cadmium, and barium. The release did not contain mercury. The plume also generated 15,000 kg of dissolved forms of these metals as it initially traveled through Cement Creek. Both dissolved and colloidal/particulate metals can be toxic, varying by beneficial uses, organisms, and length of exposure and were a concern as the Gold King plume travelled downriver.

What happened to the metals released from the Gold King Mine?

The Gold King release traveled downstream through the Animas River and joined the San Juan River on August 8. The plume traveled for an additional 4 days before entering Lake Powell in Utah nearly 550 kilometers from the Gold King source. Metals mass in the plume travelled as a coherent plume of metals over a period of 8 days traveling at approximately 3 kilometers per hour.

For most of the metals mass in the plume to pass a location required from 20 hours near the Gold King source up to 60 hours in the lower river, lengthening due to drag forces of the river bed. However, the majority of the metals mass and highest concentrations travelled within a core 12-hour period, a length of time that persisted through much of the length of the river. Evidence suggest that within the core of the plume there was a front of dissolved metals pushed in front of the acidity and trailed by precipitated iron and aluminum oxides that created the intense yellow color and turbidity.

Once the acidic plume entered the larger and more alkaline Animas River, both dissolved and colloidal/particulate metals concentrations began to decline rapidly as chemical reactions and hydraulic processes transformed, diluted and deposited material.

Dilution from incoming flow to the river from the Animas and other tributaries diluted concentrations almost as soon as they entered the Animas. Upon joining the Animas, flow was diluted by 50% and by the time the plume traveled 4 kilometers it was diluted to 10% of its original strength by the incoming Mineral Creek. The plume was diluted to just 1% of original strength by the time it reached Durango 95 km from source.

Geochemical reactions neutralized the low pH and transformed dissolved metals to iron and aluminum oxides, among other minerals. Particles were probably initially colloidal (solids of small size, less than 10 µm), suspended in the water (e.g. paint and milk are colloids). Acid neutralization triggered formation of iron and aluminum oxides and other incipient minerals through chemical reactions that produced the intense yellow color of the river. Formation of oxides occurred primarily as the plume moved from Silverton to below Durango where the acidity was largely exhausted. Geochemical calculations of neutralization were supported by observations of pH along the river and reduction of dissolved metals was observed in water samples collected as the plume passed.

The volume of acidity in the release carried dissolved metal ions much farther downstream in dissolved form than typically occurs with the ongoing contamination. The aluminum and iron oxides scavenged dissolved trace metal into their structures removing them from solution as well. Dissolved metals concentrations were at background levels by the time the Animas joined the San Juan River 190 km from the Gold King mine.

Metals concentrations in the water also declined as colloidal/particulate metals including entrained particulates and aggregated iron and aluminum oxides were deposited in the river bed. Metals mass was deposited along the entire length of the Animas River at channel margins and behind channel roughness. However, there were significant depositional areas where most of the mass dropped out. The most significant deposits were estimated to occur in the upper Animas River in the 75 km reach between Silverton and Durango, with a majority depositing where the river exits the constrained channel reach through the San Juan Forest at Bakers Bridge (64 km from source) and enters into the next 30 km of braided and meandering river segments north of Durango. Another important depositional area was between 132 and 164 km from source in the lower Animas River near Cedar Hill and Aztec, NM.

The GKM plume continued to flow from the Animas into the sediment-rich San Juan River at Farmington, NM. The modeling estimated that between 45,000 to 75,000 kg of colloidal/particulate metals mass was carried from the Animas River into the San Juan River at Farmington, NM. The plume that entered the San Juan was largely iron and aluminum but still carried a relatively high mass of lead, copper, zinc and manganese.

Although Animas River metals concentrations were measurably high with the Gold King plume, the plume became difficult to distinguish once it entered the Animas River. The two rivers were about equal in flow but the San Juan River had a very high amount of sediment with commensurate high background loads of metals naturally present in the sediment.

When the Gold King plume mixed with the large existing sediment load in the San Juan River, the metals concentrations became largely comparable to those in the San Juan. Important exceptions were lead and to a lesser extent zinc and selenium. Although the San Juan River background sediment metal concentrations are generally low, the river carries so much sediment during storms and high flow events that water quality appears to be strongly related to sediment concentrations. Overall metal concentrations in the streambed of the San Juan River are much lower than they are in the Animas River and increase proportionately with flow during storms as the sediments in the San Juan River are mobile in high flows.

Modeling analysis estimated that 20 to 30% of the remaining Gold King mass deposited in the 250 km of the San Juan River before it flowed 250 into Lake Powell in Utah (approximately 20,000 kg). Measurements of streambed sediments suggests that metals tended to increase in the streambed sediments relative to background downstream of the confluence of the Animas and San Juan Rivers, especially within the first 10 km.)

How was water and sediment quality affected by the Gold King Mine release?

Metals in the Surface Water

Metals are natural components of soils and present in minute quantities in water. High levels of metals can be detrimental to human, terrestrial, and aquatic life. States and tribes have adopted water quality criteria that identify safe concentrations that protect life ingesting or exposed to water in various ways, such as drinking, recreational contact, and irrigation. Criteria also specific safe levels for aquatic life.

Generally, dissolved metals are considered more toxic, more reactive, and more mobile than particulate metals. While dissolved metals initially increased in Cement Creek, they decreased to nearly pre-event conditions by the time the plume flowed from the Animas and had minimal impact on the San Juan River. Most of the metals concentration in the plume was colloidal/particulate solids. These can also have toxicity, and water quality criteria for some beneficial uses reference total concentrations (dissolved + particulates passing a 45 micron filter). Aluminum is a prominent example that was very abundant in the Gold King plume. Total metals are also the basis for domestic supply and recreational contact.

Potential adverse impacts from exposure to high metals concentrations in water was assessed by comparing modeled plume concentrations to appropriate state or tribal water quality standards as the plume moved through the length of the river.

Water quality criteria defined for various water uses were exceeded in some locations as the plume passed, especially in the upper Animas River closer to the mine source. The duration of water quality exceedances was short as the plume moved quickly, varying by metal. Importantly, most metals did not exceed any criteria at any location. Agricultural criteria for copper, lead, and manganese were exceeded to 132 kilometers from source, including Durango and the Southern Ute Indian Tribe reservation. The EPA coordinating with states, tribes and local municipalities curtailed the use of water for drinking, irrigation, livestock watering, and recreation as the plume for a number of days to prevent exposures. Dilution and chemical reactions largely limited the spatial extent of significantly elevated concentrations to the upper Animas River.

Because of the short duration of the plume, aquatic life were more vulnerable to acute, shorter term concentrations during movement of the plume itself. Acute criteria for aquatic life for aluminum were exceeded for up to 6 hours in the Animas River to the Colorado border at 147 kilometers from source. The duration was less than the 96 hour exposure built into the criteria. There were no reported fish kills and post event surveys by a variety of organisms have indicated other aquatic life did not appear to have suffered harmful effects from the plume. No fish kills were reported from numerous surveys conducted after the event. Bioaccumulation modeling conducted in this study support that fish and aquatic biota likely took up metals as the plume passed but excreted it over the next 15 days without lasting harmful effects to the organisms.

Monitoring continues to determine if there will be longer term chronic impacts from deposited metals beyond the effects of acid mine drainage known to impair parts of the watershed from historic mining activity. Concentrations of aluminum and iron surpassed Colorado water quality standards to protect aquatic life from persistent, long-term exposure. Similarly high levels of these metals have occurred in the Animas River during spring runoff in previous years as well. The Mountain Study Institute located in Durango Colorado has studied the aquatic life in the Animas River since the Gold King plume. A 2016 report found no substantial impacts to aquatic communities that signal degrading water quality.

The metals that may have had the largest effect on water quality were aluminum, lead, and iron due to their predominance in the release load. These metals were particularly abundant in the plume and triggered exceedances of one or more water quality criteria along the rivers. Variation in exceedances reflect differences in criteria among states and tribes. Particulate (total) lead was detected most frequently.

Bed Sediments

Gold King plume mass could have been deposited throughout the length of affected rivers, and there are many reports and photographs of residue along the length of the Animas River. Although al large amount of Gold King material was deposited, especially in the headwaters, the metals deposits were not different in the content and mass from those already in the streambed that store the legacy of a century of mining and ongoing AMD contamination. Metals concentrations in streambed sediments was not statistically different from pre-event conditions where there was sufficient data to compare.

Post plume adjustments to the chemistry of the deposited minerals could be expected. The deposited precipitates were likely a mix of incipient and more stable minerals with different degrees of chemical stability. Deposits were not sampled for their geochemistry and mineralogy that would provide this study more complete understanding of the post event chemistry. Some of the minerals that probably formed, such as gypsum (a calcium sulfate mineral), would likely to dissolve under different pH conditions. The majority of the deposits were likely iron and aluminum oxides. Once deposited, these would undergo "aging" and ripening as their structure internally organizes toward long term chemical stability.

Have Water and Metal Concentrations Returned to Pre-Event Levels?

It has been an ongoing concern that deposited metals would degrade water quality after the plume passed, or that deposited plume sediments would remobilize during higher flows and generate a second wave of contamination through the system. EPA, states, and tribes have monitored water and sediments intensively in the months following the release to evaluate post-event effects.

Water concentrations in the Animas River declined towards background conditions within hours to days after the Gold King plume passed documented by monitoring during the plume period.

An intensive monitoring program sampling water and sediment of the Animas and San Juan Rivers began during passage of the Gold King plume and has continued in the year following the release to understand its long term impacts. Nearly 1,400 water quality samples have been collected to date. Most of the post-event samples were collected from August through October 2015 with a hiatus during the winter. Sampling resumed in February 2016 and included focused efforts to sample spring snowmelt from May through June 2016. Various studies, monitoring programs, and routine sampling at USGS gages have generated historic data for metals concentrations in water and sediment in the Animas and San Juan Rivers prior to the Gold King release. These data allowed for pre- and post-comparisons to assess the effect and recovery of the system to pre-existing conditions.

Water concentrations declined to background conditions for many metals of interest in all reaches of the Animas River south of Silverton and in the San Juan River soon after the Gold King plume passed. In the headwaters of the Animas River, water quality continues to be impaired by acid mine drainage in the watershed above Silverton. Water chemistry has changed somewhat since the Gold King plume and treatment, but high concentrations of metals continue to flow from Cement Creek into the Animas River.

Downstream of Silverton, the Animas River metals of greatest concern such as lead, arsenic, copper, zinc, and cadmium have remained comparable to pre-event levels during the fall period following the release, accounting for the strong effect of flow on metal concentrations during this period. Where pre-event data was available for statistical comparison, there were no significant changes in these metals at any location in the Animas or San Juan Rivers through the fall months following the release. However, statistical analyses indicate that post event geochemical reactions are taking place within the metal deposits left by the plume, primarily involving iron and aluminum that make up most of the mass, There have been persistent changes in iron and aluminum that manifested in dissolved and total concentrations at various locations within the Animas and San Juan Rivers in both surface water and bed sediments.

Iron and aluminum concentrations have historically been high in the headwaters of the Animas as evident in pre-event data. Most of the Gold King release mass that flowed through the rivers was Fe and Al (88.3 and 8.4% respectively) occurring predominantly as colloidal/particulates but with a dissolved fraction as well.

In the mid Animas, metals in the streambed and water have declined somewhat from historical levels, suggesting that deposited aluminum and iron oxides continue to scavenge metals from the water. Concentrations of some trace metals in the Durango area have declined relative to historic levels, and improved water quality.

In the lower Animas, Gold King deposits appear to be shedding low but elevated concentrations of dissolved aluminum and iron into the Animas River as concentrations in the water column are elevated relative to pre-event conditions. Adjustments are small but statistically detectable and well below water quality criteria thresholds. The dissolved metals from the lower Animas subsequently move into the San Juan River where they have increased concentrations in proportion to Animas flow. Once in the San Juan, the dissolved aluminum and iron are conserved and appear to pass through the length of the San Juan without change of deposition. On average iron and aluminum changes have not increased metals to adverse levels relative to water quality criteria applicable to the San Juan River. They also have not affected the concentrations of other trace metals to a detectable level.

Groundwater Effects

There are hundreds of water supply wells in the floodplain aquifers of the Animas River, ranging from continuous larger pumping wells (the community wells) to the small pumpers (the domestic/household wells). There are also intermittent intermediate pumpers (the irrigation wells). Groundwater modeling suggests only a handful of these wells potentially source from the Animas River and were potentially vulnerable to exposure to the GKM river plume. Given their low pumping rates, the domestic/household wells would most likely need to be located in proximity to a losing reach of the river. The complication is whether any given stretch of the Animas River is either gaining or losing is site specific and temporal. One community well located within 35m of the mid Animas River floodplain near Baker's Bridge had a chemical signal of some dissolved metals; we could not reject the hypothesis that this signal may have been associated with the GKM plume.

Remobilization of Gold King Deposits

Gold King metals deposited throughout the Animas system, with most settling in the mid and upper Animas but deposition also occurred in the lower Animas, especially between RK 150 and RK 180. Water and sediment concentrations were elevated in the lower Animas, and post event adjustments immediately following the plume showed elevated concentrations in water and sediments that declined in the first several weeks after the release. A large storm 3 weeks after the release effectively swept the deposits from the lower Animas, which then maintained low sediment concentrations until the following spring snowmelt when they sediments appeared to respond to upstream sediments. Water concentrations in the lower Animas were responsive to a series of storms through the fall, but declined to low levels between storms.

The middle and upper Animas did not have storms of sufficient magnitude to mobilize the Gold King deposits until the 2016 spring snowmelt. Water and sediment was sampled over a six week period in May and June of 2016 capturing the effect of the snowmelt hydrograph at many locations along the Animas and San Juan Rivers. Flow was particularly high in the headwaters of the Animas River where preliminary gage data suggested that peak runoff was the second highest recorded since 1991 and the largest since 1995. Daily metals loading models were developed for the study using average flows at the gages and historically available data to build regressions between flow and metals concentrations that could be used to estimate annual metals from at various locations in the river. Dissolved metals tend to decrease with increased flow, suggesting dilution, while particulate metal concentrations tend to increase with flow reflecting particle transport mechanics.

Field measurements of water and sediment during the 2016 snowmelt hydrograph indicated that Gold King deposits were mobile during snowmelt. Elevated concentrations of metals could be detected in the water and sediments at most locations during 2016 snowmelt. Metals concentrations would be naturally elevated during peak runoff, but field evidence and modeling suggested that at least some of the increase was probably resuspended Gold King deposits. Updated 2016 metals data input to those models predicted small increases in metals concentrations that when factored over the duration of snowmelt runoff accounted for mobilization of all of the mass deposited in the Gold King plume. The empirical daily load models agreed closely with modeling predictions based on hydraulics mobilization and transport of deposited material.

Gold King deposits appeared to mobilize from the upper and mid Animas River relatively early on the rising limb of the 6-week snowmelt hydrograph. This was especially evident at the sampling location at RK 64 which received some of the heaviest deposits during the plume. Metals increased in sediments for a time at Durango that may have received them from upstream. The additional metals were removed at the peak of the hydrograph. Whether this pattern persisted through the lower Animas as only one sample collected near the peak of snowmelt was available. Elevated metals were seen in the water and sediments into the San Juan system. Concentrations were commensurately lower than in the Animas but could be detected.

The next round of sampling will help to clarify whether Gold King deposits moved out of the entire system, or whether some lagged behind settling on the falling limb of the hydrograph.

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APPENDICES

In separate files for review

- **A) Acquired Data Sources**
- **B) WASP Application and Calibration**
- **C) Geochemistry Analysis**
- **D) Groundwater Model Application and Calibration**
- **E) Bioaccumulation Model Application**
- **F) Quality Assurance and Quality Control**

GLOSSARY

(numbers in parentheses are references at end of glossary)

Acid mine drainage: Drainage of water from areas that have been mined for coal of other mineral ores. The water has a low pH because of its contact with sulfur-bearing material and is harmful to aquatic organisms. (2)

Adit: A horizontal or gently inclined excavation made into the side of a hill or mountain to provide underground access. Adits commonly are driven with an uphill slope (about 1%) to provide drainage such that groundwater seepage will readily flow out of the excavation and discharge to the surface. An adit is only open to the ground surface on one end, the other end may be a dead end or it may connect to a shaft, raise or other type of mine passage that could eventually reach the ground surface. (9)

Advection: Movement of mass resulting from unidirectional flow; moves mass from one position in space to another (10)

Analysis of existing data: The process of gathering and summarizing existing data from various sources to provide current information on hydraulic fracturing activities. (8)

Aquifer: An underground geological formation, or group of formations, containing water. A source of groundwater for wells and springs. (2)

Blowout: A sudden, violent, release of gas or liquid due to the reservoir pressure in a drill hole or mine. (9)

Caldera: a large depression formed in volcanic rock with an approximately circular shape. (9)

Contaminant: A substance that is either present in an environment where it does not belong or is present at levels that might cause harmful (adverse) health effects. (2)

Colloid: A homogenous, non-crystalline substance consisting of large molecules or ultramicroscopic particles of one substance dispersed through a second substance. Colloids include gels, sols, and emulsions; the particles do not settle and cannot be separated out by ordinary filtering or centrifuging like those in suspension. Range in size from 10—6 to 10-3 cm.

Conveyance loss: Water lost in transit from a pipe, canal, conduit, or ditch by leakage or evaporation. Generally, the water is not available for further use; however, leakage (e.g., from an irrigation ditch) may percolate to a groundwater source and be available for further use. (6)

Diffusion: movement of mass due to random water motion or mixing, moves mass from regions of high concentration to low concentration (10)

Dispersion: the spreading of mass due to velocity differences in space (10)

Dissolved analyte: The concentration of analyte in an aqueous sample that will pass through a 0.45 µm membrane filter assembly prior to sample acidification (Section 8.2). (1)

Domestic water use: Water used for indoor household purposes such as drinking, food preparation, bathing, washing clothes and dishes, flushing toilets, and outdoor purposes such as watering lawns and gardens. Domestic water use includes water provided to households by a public water supply (domestic deliveries) and self-supplied water. (6)

Drinking water resource: Any body of water, ground or surface, that could (now or in the future) serve as a source of drinking water for public or private water supplies. (8)

Equilibrium: the state of dynamic balance attained in a reversible chemical reaction when the velocities (of reaction progress) in both directions are equal. (12)

Empirical: Based on observations

Formation: A geological formation is a body of earth material with distinctive and characteristic properties and a degree of homogeneity in its physical properties. (2)

Formation water: Water that occurs naturally within the pores of rock. (5)

Freshwater: Water that contains less than 1,000 milligrams per liter (mg/L) of dissolved solids. Generally, water with more than 500 mg/L of dissolved solids is undesirable for drinking and many industrial uses. (6)

ft^3/s: An abbreviation for cubic feet per second, a unit of measure for rate of flow. One cubic foot per second of flow is equal to 448.83 gallons per minute. (9)

gpm: An abbreviation for gallons per minute, a unit of measure for rate of flow. (9)

Geographic information system (GIS): A computer system designed for storing, manipulating, analyzing, and displaying data in a geographic context, usually as maps. (2)

Groundwater: All water found beneath the surface of the land. Groundwater is the source of water found in wells and springs and is used frequently for drinking. (2)

Hydraulic Bulkhead: A structural barrier placed in a mine or tunnel for the purpose of impounding water to flood the mine openings and re-establish the pre-mining groundwater levels. The terms adit plug, mine plug, mine seal, and bulkhead seal also have been used to describe this type of impounding structure. (9)

Hydraulic gradient: Slope of a water table or potentiometric surface. More specifically, change in the hydraulic head per unit of distance in the direction of the maximum rate of decrease. (2)

Industrial water use: Water used for fabrication, processing, washing, and cooling. Includes industries such as chemical and allied products, food, paper and allied products, petroleum refining, wood products, and steel. (6)

Instream use: Water that is used, but not withdrawn, from a surface water source for such purposes as hydroelectric power generation, navigation, water quality improvement, fish propagation, and recreation. (6)

Irrigation water use: Water that is applied by an irrigation system to assist crop and pasture growth, or to maintain vegetation on recreational lands such as parks and golf courses. Irrigation includes water that is applied for pre-irrigation, frost protection, chemical application, weed control, field preparation, crop cooling, harvesting, dust suppression, leaching of salts from the root zone, and conveyance losses. (6)

Iron-oxide: A general term for a group of oxidized minerals and amorphous compounds that form in nature due to the weathering of iron-containing rocks and minerals and due to the oxidation of iron-rich waters. It can include minerals such as goethite, lepidocrocite, ferrihydrite, schwertmannite, jarosite, and colloids such as limonite (Wolkersdorfer, 2008). In mine workings it commonly precipitates out, forming sediment composed of orange-brown colloidal-sized particles. These iron minerals have a strong affinity for absorbing metals such as cadmium, lead, arsenic, and other elements when they form. The terms “yellow boy” and “ochre” commonly used in reports about abandoned mines refer to the same material. (9)

Livestock water use: Water used for livestock watering, feedlots, dairy operations, and other on-farm needs. Types of livestock include dairy cows and heifers, beef cattle and calves, sheep and lambs, goats, hogs and pigs, horses and poultry. (6)

Major cations: For purposes of this report includes calcium (Ca), magnesium (Mg), potassium (K) and sodium (Na).

Mechanistic: Based on physical processes

Method blank: An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The method blank is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus (1)).

Method detection limit (MDL): The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence. The MDL is determined according to procedures described in 40 CFR Part 136, Appendix B. (1)

Mine: A surface or underground excavation made for the purpose of extracting a valuable mineral commodity such as coal or metal ore. (9)

Partition Coefficient: The ratio of concentrations of a constituent (e.g., metal) between two phases (e.g., solid phase and water) (10).

Partitioning: The tendency for a constituent to attach to particles (10).

Permeability: Ability of rock to transmit fluid through pore spaces. (1)

Porosity: Percentage of the rock volume that can be occupied by water. (1)

Portal: A structure constructed at the entrance to an adit or tunnel for the purpose of providing support to the surrounding soil and weathered rock in order to allow safe passage into the underground mine opening. (9)

Public supply water use: Water withdrawn by public and private water suppliers that furnish water to at least 25 people or have a minimum of 15 connections. Public suppliers provide water for a variety of uses, such as domestic, commercial, industrial, thermoelectric power, and public water use. (6)

Public supply deliveries: Amount of water delivered from a public supplier to users for domestic, commercial, industrial, thermoelectric power, or public-use purposes. (6)

Public water system (PWS): A system that provides water to the public for human consumption through pipes or other constructed conveyances. A PWS, per EPA's definition, must have at least 15 service connections or regularly serve at least 25 people. (2)

Public water use: Water supplied from a public supplier and used for such purposes as firefighting, street washing, flushing of water lines, and maintaining municipal parks and swimming pools. Generally, public-use water is not billed by the public supplier. (6)

Resuspension: the velocity of particles leaving the sediment layer and entering the water column

Safe yield: Commonly used in efforts to quantify sustainable groundwater development. The term should be used with respect to specific effects of pumping, such as water-level declines, reduced streamflow, and degradation of water quality. (7)

Saturation: the state of a solution when it holds the maximum equilibrium quantity of dissolved matter at a given temperature. (11)

Self-supplied water use: Water withdrawn from a groundwater or surface water source by a user rather than being obtained from a public supply. (6)

Settling: The velocity of particles moving down the water column towards the sediment layer

Shaft – A vertical or steeply inclined excavation from the surface extending down into the ground for the purpose of providing underground access. Related terms are winze and raise. A winze is a similar downward extending excavation but it is initiated from within an underground mine working and therefore is not open to the ground surface. A raise is an upward extending excavation initiated from within an underground mine working. A raise may or may not extend to the ground surface. (9)

Source water: Water withdrawn from surface or ground water, or purchased from suppliers, for hydraulic fracturing. (8)

Solid sample: A sample taken from material cloassified as either soil, sediment, or industrial sludge. (1)

Statistical analysis: Analyzing collected data for the purposes of summarizing information to make it more usable and/or making generalizations about a population based on a sample drawn from that population. (2)

Stope – An underground excavation from which ore has been removed. (9)

Surface water: All water naturally open to the atmosphere (rivers, lakes, reservoirs, ponds, streams, impoundments, seas, estuaries). (2)

Total dissolved solids: The quantity of dissolved material in a given volume of water. (2)

Total recoverable analyte: The concentration of analyte determined either by "direct analysis" of an unfiltered acid preserved drinking water sample with turbidity of <1 NTU, or by analysis of the solution extract of a sludge, solid, or unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method. (1)

Tuff – A volcanic rock formed of consolidated or cemented volcanic ash. (9)

Tunnel: A horizontal or gently inclined excavation that penetrates a hill or mountain and is open to the surface on both ends such as a highway tunnel or railroad tunnel. The term tunnel is commonly misused in mining to refer to long adits. For example, the American Tunnel is actually an adit because it does not extend to the opposite side of the mountain. (9)

Water use: Pertains to the interaction of humans with and influence on the hydrologic cycle; includes elements such as water withdrawal, delivery, consumptive use, wastewater release, reclaimed wastewater, return flow, and instream use. (6)

Waste-Rock Dump – A pile of rock and soil placed onto the ground surface immediately outside of a mine entrance as a means of disposal of unwanted material that must be broken and excavated to gain access to the ore in the mine. (9)

Water sample: A sample taken from one of the following sources: drinking, surface, ground, storm runoff, industrial or domestic wastewater. (1)

Watershed: An area of land that drains to a particular stream or river. (9)

Water withdrawal: Water removed from the ground or diverted from a surface water source for use. (6).

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